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The Mercury Photosensitized Reactions of Ethylene

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An investigation has been made of the mercury ($^3P_1$) photosensitized reactions of ethylene. In addition to hydrogen and acetylene the main products are butene, butane and hexenes. The variation of the rate with the pressure of ethylene suggests that a deactivation process is involved, the initial process being of the type

$$C_2H_4+Hg(^3P_1)\rightarrow C_2H_4^*+Hg(^1S_0)$$

followed by

$$C_2H_4^*+C_2H_4\rightarrow 2C_2H_4$$

or

$$C_2H_4^*\rightarrow C_2H_2+H_2.$$

Polymerization arises largely by a free radical mechanism and butane is formed by the reactions

$$H_2+Hg(^3P_1)\rightarrow 2H+Hg(^1S_0)$$
$$H+C_2H_4\rightarrow C_2H_5$$
$$2C_2H_5\rightarrow C_4H_{10}.$$

The mechanism is shown to be consistent with the value found for the quantum yield.

INTRODUCTION

ALTHOUGH a considerable number of papers have been published on the mercury photosensitized reactions of ethylene,[1-7] very little is known about the mechanism. There seemed to be fairly general agreement, however, that the initial step is the formation of acetylene and hydrogen, and that this is followed by the polymerization and hydrogenation of the acetylene. Such postulates were natural in view of the initial pressure rise and the well-known ease with which acetylene is polymerized by excited mercury.[6] The results which we have obtained, being of a more quantitative nature, throw additional light on the first postulate but necessitate a somewhat different mechanism to account for the subsequent pressure decrease.

STATIC RUNS

Both static and circulating runs were made, as well as a few in which a single pass flow method was used. The static system is shown in Fig. 1.

The quartz mercury "resonance" lamp L was bent in the form of a spiral in order to obtain a fairly intense source and was mounted in a

[1] A. R. Olson and C. H. Meyers, J. Am. Chem. Soc. **48**, 389 (1926).
[2] H. S. Taylor and J. R. Bates, Proc. Nat. Acad. Sci. **12**, 714 (1926).
[3] A. R. Olson and C. H. Meyers, J. Am. Chem. Soc. **49**, 3131 (1927).
[4] J. R. Bates and H. S. Taylor, J. Am. Chem. Soc. **49**, 2438 (1927).
[5] H. S. Taylor and D. G. Hill, J. Am. Chem. Soc. **51**, 2922 (1929).
[6] H. W. Melville, Trans. Faraday Soc. **32**, 258 (1936).
[7] J. C. Jungers and H. S. Taylor, J. Chem. Phys. **6**, 325 (1938).

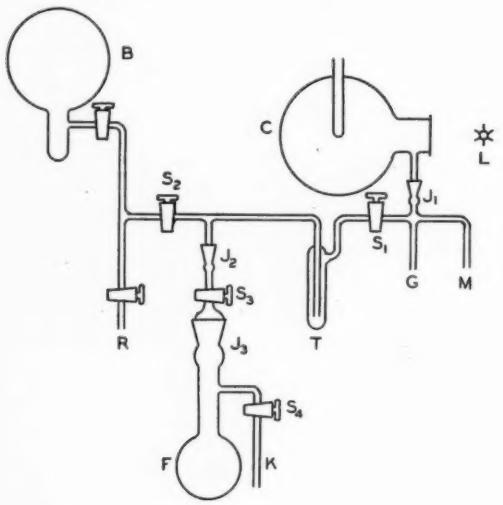

FIG. 1.

water thermostat to ensure a constant operating temperature (25°C). The radiation from the lamp passed out of the thermostat through a quartz window in front of which the cell, *C*, was mounted. Most of the energy emitted by the lamp was concentrated in λ2537A. In view of the fact that the light path included the spiral of the lamp, the window of the thermostat and the window of the cell, all of which were of fused quartz, as well as several centimeters of distilled water and a centimeter or two of air, it can safely be assumed that the intensity of any resonance radiation of λ1849A reaching the cell would be quite negligible.

Three different static cells were used. They could be removed from the rest of the system at the ground joint, J_1, to facilitate cleaning, and then replaced in their original position. Temperatures could be read on thermometers inserted in the thermometer wells extending into the cells. To avoid temperature fluctuations the cells were surrounded, with the exception of the windows, with a thick layer of cotton wool. All pressure readings were corrected back to 25°C. For the cells S_1 and S_3 the volumes of the system, including the manometers, were 3400 cc and 644 cc, respectively. An accurate calibration for the third cell, S_2, was not required. The volumes of the cells and the incident light intensities were such as to prevent the occurrence of high concentrations of products in any one part of the cell. Interrupting a run in the middle and then continuing it several hours later made no apparent difference, indicating that diffusion of the products away from the reaction zone was sufficiently rapid and that there was no diminution of mercury pressure as a result of mercury being used up in the reaction, as found by Melville[6] in the mercury photosensitized polymerization of acetylene.

The cells contained a few drops of pure mercury to supply the necessary vapor for absorbing the resonance radiation. Since all experiments were performed within a degree or two of 25°C the mercury vapor pressure was about 1.8×10^{-3} mm.

Pressures were measured either by the McLeod gauge, *G*, or the U-tube manometer, *M*, depending on their magnitude. The cathetometer used in conjunction with the U-tube manometer enabled the pressures to be measured to an accuracy of ±0.02 mm but this accuracy was only obtained by illuminating the mercury surface as recommended by Glazebrook.[8]

The system was connected to the usual liquid-air trap, McLeod gauge, blow-off tube, mercury pump and Hyvac at the point *R*.

After filling the system to the required pressure it was isolated by closing the stopcock, S_1, and left at least six or seven hours, or usually over night, to enable the mercury vapor pressure to attain its equilibrium value. After illumination, the non-condensible gas could be pumped off through S_1 and S_2, the condensible gas being trapped out with liquid air in the trap, *T*. Acetylene was determined by transferring the condensible gas from *T* to the evacuated bulb, *F*, which was cooled in liquid air. S_3 was then closed and *F* removed from the rest of the system at the ground joint, J_2. The method of Ross and Trumbull[9] was used in the determination of acetylene. Neutral 2.5 percent silver nitrate solution was sucked into *F* by inserting the side tube, *K*, in a flask containing the solution and then opening S_4. After thorough shaking, the large ground joint, J_3, was opened and the liberated nitric acid titrated directly in *F* using *N*/10 sodium hydroxide and back-

[8] *Dictionary of Applied Physics*, Vol. III, p. 151.
[9] W. H. Ross and H. L. Trumbull, J. Am. Chem. Soc. **41**, 1180 (1919).

titrating with $N/10$ hydrochloric acid, after precipitating the excess silver with neutral sodium chloride. Blanks were run regularly. A brom cresol green-methyl red indicator was used. The quantity of 2.5 percent silver nitrate used was found to be important. 50 cc of this solution was sufficient for an accurate determination of acetylene in quantities up to 6 or 8 cc of gas at N.T.P. For larger amounts correspondingly larger volumes of solution were necessary. The ethylene itself did not react with silver nitrate.

Circulating Runs

The arrangement of the apparatus is shown in Fig. 2. The stainless-steel bellows pump, P, operated by a Bodine type NSY-12-RH synchronous motor was used to circulate the gas in the direction of the arrows. The bellows, obtained from the Chicago Metal Hose Company, was 12″ long and $2\frac{3}{4}$″ O.D. but a solid steel plunger welded to the bottom end and extending almost to the top eliminated most of the dead space. Although the synchronous motor and self-contained reducing gears operated at 30 r.p.m., the pumping speed could be varied by adjusting the position of the movable arm where it was fastened to the rotating wheel. Thus, with contact being made at $\frac{1}{4}$″, $\frac{3}{8}$″, $\frac{1}{2}$″ and $\frac{5}{8}$″ from the center of the wheel, circulating speeds of approximately 1000, 2000, 3000 and 3800 cc per minute were obtained. These speeds were measured with the circulating gas at atmospheric pressure. Because of the constant slight head of mercury in the valves, V, the speeds would be somewhat less than this at the lower pressures used in the circulating runs but satisfactory circulation was obtained at pressure down to 50 mm or less. Because the reduced pressure tended to contract the bellows, counterbalancing weights were suspended on a yoke fastened to the moving end of the bellows.

The gas was saturated with mercury vapor by passing over hot mercury (circa 45°C) in the trap, T_4. Subsequent passage over fine iron gauze in the de-saturator, D, ensured that the mercury vapor pressure would not be higher than about 1.8×10^{-3} mm. D could be immersed in ice water if necessary. After passing through the lamp-cell, L,[10] the higher products were collected in the trap, T_1. This trap was immersed in mercury contained in a double-walled vessel and was kept cold by liquid air contained in the large vacuum flask. By regulating the current supplied to a heater immersed in the mercury the temperature of the trap could be controlled within a couple of degrees as indicated by a thermocouple soldered to a thin brass sheet in the bottom of the trap. The pressure in the apparatus was measured by the manometer, M_1. The volume of the lamp-cell itself was about 1600 cc. Additional volume was obtained by inserting the flask, F, the volume of the whole system being 4750 cc. The customary McLeod gauge, blow-off tube, liquid-air trap, mercury-vapor pump and Hyvac were connected at K.

Gaseous products could either be transferred to a gas holder by means of a Toepler pump, or the trap, T_1, could be cooled to the temperature of liquid air, S_2 closed, and all condensible gas and liquid products collected, the non-condensible gas being pumped off at N. With S_1 closed the condensible products were then transferred to a tube cooled with liquid air and connected to the system at the ground joint, J. In either case the products were then transferred to a low temperature still of the Podbielniak type. Liquids above butene were fractionated on a similar still adapted for high temperatures. Acetylene was determined by analyzing an aliquot of the gas taken at the end of a run.

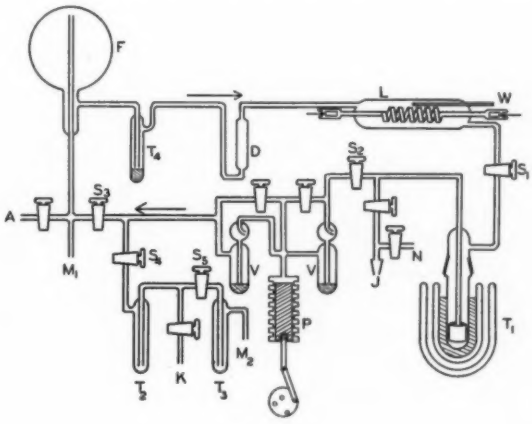

Fig. 2.

[10] E. W. R. Steacie and N. W. F. Phillips, Can. J. Research **B16**, 219 (1938).

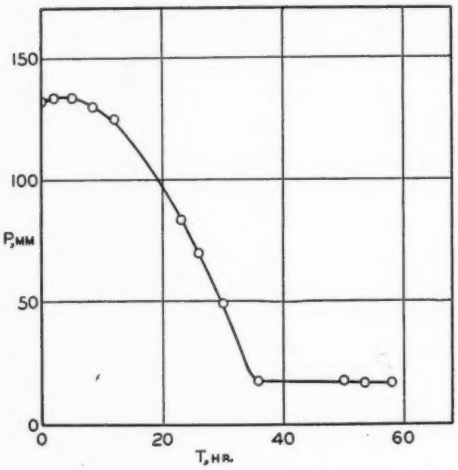

FIG. 3. Pressure *vs.* time for a typical static run.

The procedure was the same as described under "Static Runs" except that the pressure of the gas and the volume of the flask, F (Fig. 1), had to be taken into consideration.

SINGLE PASS RUNS

A few runs were made in which the ethylene was passed through the system (Fig. 2) only once. This was done with the intention of avoiding subsidiary reactions of the products as much as possible. The gas was introduced through a fine capillary at A. With S_3 closed, the gas passed through the apparatus in the direction of the arrows and the condensible gas not collected in T_1 was condensed in T_2 which was cooled with liquid air. Products collected in T_1 were removed in the same manner as in the circulating runs. "Non-condensible" gas was collected in the trap, T_3, which was filled with activated charcoal and cooled with liquid air. On closing S_5 and warming T_3 to room temperature the pressure of non-condensible gas could be measured on the manometer, M_2, and knowing the effective volume of T_3 the quantity of gas could be calculated. It could then be removed by a Toepler pump and analyzed by combustion.

COMBUSTION APPARATUS

Non-condensible gas was analyzed by combustion in an apparatus similar to that used by Steacie and Phillips, reference 10, p. 303. After combustion on a hot platinum spiral in a 2-liter flask in the presence of an excess of oxygen, the remaining oxygen was pumped off through a small trap cooled with liquid air. On isolating the trap and letting it warm to room temperature the pressure of carbon dioxide (plus water vapor) was read on a mercury manometer. The apparatus was improved by connecting an oil manometer to the large combustion bulb. On expanding the carbon dioxide and water back into this bulb the water-vapor pressure was less than its vapor pressure at room temperature and hence the total pressure of the products of combustion could be read on the oil manometer. The carbon dioxide was pumped off through the same trap cooled with a dry-ice-acetone mixture and the pressure of water measured after expanding it back into the combustion bulb. In this way the empirical formula of the original gas was obtained.

MATERIALS

The ethylene used in these experiments was obtained from the Ohio Chemical and Mfg. Co. and was stated to be 99.5 percent pure. The gas taken from the steel cylinders was found to contain about $\frac{1}{4}$ percent of non-condensible gas and on combustion this was shown to be free from both carbon and hydrogen, indicating that the impurity is probably air. A very small trace of a hydrocarbon of fairly high molecular weight was found. There was no measurable amount of propylene present. Before use the ethylene was freed of dissolved air by the usual freezing and pumping technique and higher hydrocarbons were eliminated by bulb to bulb distillation, only the middle fractions being retained.

The purified ethylene was stored in a small, style "A" cylinder with a specially designed

TABLE I. *Static runs.*

RUN	CELL	P_0 mm	ΔP_{max} mm	RUN	CELL	P_0 mm	ΔP_{max} mm
98	*S*1	0.19	0.09	90	*S*3	5.27	0.68
96	*S*1	0.31	0.09	89	*S*3	8.09	0.94
102	*S*1	0.41_6	0.17_5	81	*S*3	14.66	1.44
97	*S*1	0.55	0.15_6	77	*S*3	15.20	1.64
92	*S*3	0.92	0.24	86	*S*3	15.28	1.53
100	*S*1	1.01	0.33	79	*S*3	15.34	1.58
104	*S*1	1.24	0.25	83	*S*3	26.94	2.14
91	*S*3	1.93	0.37	84	*S*3	49.72	2.46
				87	*S*3	81.09	2.24

long neck which made it possible to lower the cylinder into liquid air. For convenience the ethylene used in the static runs was kept in the large bulb, *B*, Fig. 1. The lower part of *B* terminated in a wide bore tube which could be immersed in liquid air to permit of further freezing and pumping off to remove dissolved air.

Results

Static runs

The results of the static runs fall into three main divisions, (1) an investigation of the shape of the pressure-time curves as a function of pressure, (2) a correlation between the initial rate of pressure increase and the initial rate of production of acetylene and hydrogen, and (3) measurements made to determine the reason for the subsequent pressure decrease.

Pressure readings in a typical run made to completion are shown in Fig. 3. The pressure rises at first, passes through a maximum and then decreases to a constant value. A series of runs was made to determine the maximum pressure increase as a function of the initial pressure. The results are given in Table I, where P_0 is the initial pressure and ΔP_{max} is the maximum pressure increase. The course of some of these runs is shown in Fig. 4. Only the runs made at the higher pressures are shown because the great range of pressures covered by the data of Table I could not be shown conveniently on a single graph.

The data of Table I have been plotted in Fig. 5. From this curve it can be seen that the fractional increase in pressure increases as the pressure is lowered, a 40 to 50 percent increase occurring at the lowest pressures.

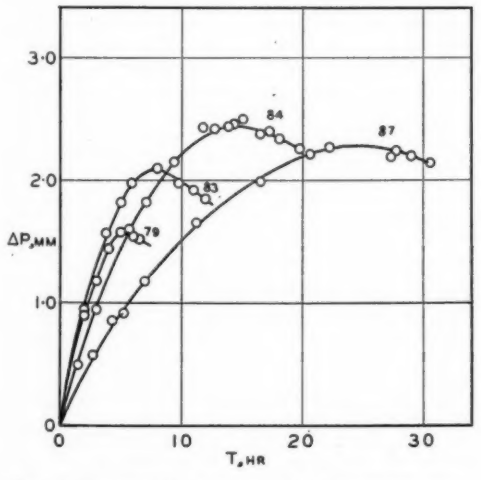

FIG. 4. Pressure increase *vs.* time for static runs.

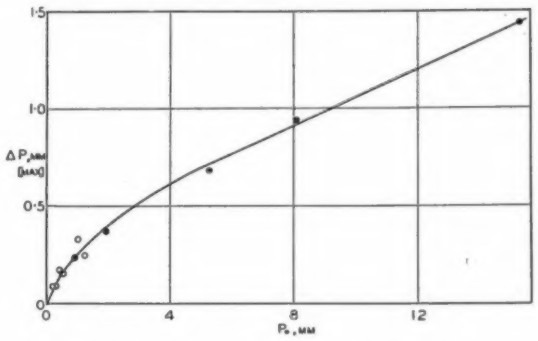

FIG. 5. Maximum pressure increase *vs.* initial pressure for static runs. ○ Runs using cell S_1; ● runs using cell S_3.

In order to determine whether the slow rate of pressure change in the neighborhood of the maximum in the high pressure runs (Fig. 4) was due to poor light transmission resulting from polymer formation on the cell window a trial run was made at 15-mm pressure without previously flaming the window to remove polymer. A rapid initial rise in pressure characteristic of the runs at low pressure showed that this was not the case.

These runs then show that not only does the maximum percentage increase in pressure decrease as the initial pressure is increased but the initial rate of pressure increase is also less at higher pressures. This latter point was investigated more thoroughly and the results are given in Table II. Only initial rates were measured in this case and they are correlated with the amounts of acetylene produced.

P_0 is again the initial pressure in mm, ΔP_{obs} is the observed pressure increase, ΔT is the duration of the run in hours, $\Delta P_{obs}/\Delta T$ is the rate of pressure increase in mm per hour, C_2H_2 is the volume of acetylene produced in cc at 25°C and 760 mm, and $\Delta P_{C_2H_2}/\Delta T$ is the rate of production of acetylene in mm per hour.

Space does not permit us to plot the pressure-time curves for each of these runs but it will be sufficient to say that when the durations of the runs were such that only a few percent of the gas was decomposed these curves were linear and with the slopes given in Table II.

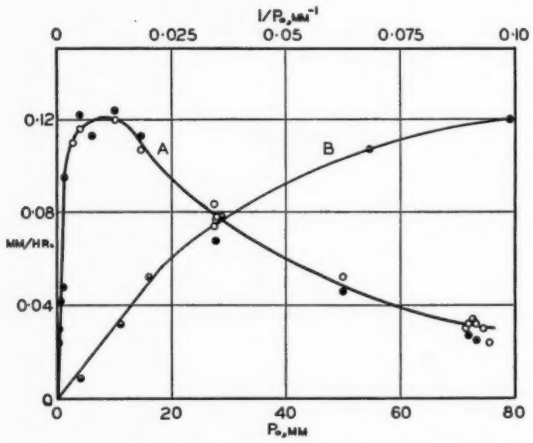

FIG. 6. ○ initial rate of production of acetylene *vs.* initial pressure; ● initial rate of pressure increase *vs.* initial pressure; ◒ initial rate of production of acetylene *vs.* reciprocal of the initial pressure. Static runs.

The results given in Table II are shown graphically in curve *A* of Fig. 6. The falling off in rates at the lower pressures is due, of course, to incomplete quenching of the resonance radiation. At the low pressure end the rate of production of acetylene is seen to be equal, within the experimental accuracy, to the rate of pressure increase. At higher pressures, however, there is evidence that although both the acetylene and the pressure increase linearly with time (in early stages), these rates are no longer equal. The possibility of thermal hydrogenation of ethylene is out of the question at the temperature used in this investigation, and in view of the fact that ethylene is just as effective as hydrogen in quenching excited mercury[11] it is highly unlikely that the difference in the rates is due to the reaction of ethylene with hydrogen atoms produced by collision of molecular hydrogen with $Hg(^3P_1)$ atoms. Also it is difficult to see how such a reaction would be favored at higher pressures. The only reasonable alternative is to postulate some sort of polymerization reaction which goes on side by side with the formation of acetylene and hydrogen.

A few runs were made to investigate the mechanism leading to the drop in pressure after the maximum is reached. The results are shown in Fig. 7. All runs were made at approximately 15-mm pressure. The one illustrated by curve *A* was interrupted when the final pressure was approximately the same as the original pressure. The pressure due to acetylene is shown by curve *D*. This shows conclusively that the assumption that the polymerization goes via acetylene is false. It appears, on the contrary, that in mixtures containing up to 30 percent or more, acetylene is relatively stable. The most likely explanation for the decrease at this stage is the reaction of hydrogen atoms with ethylene. At the time of maximum pressure the system contained almost 19 percent of acetylene and the concentration of hydrogen must be such that it would quench an appreciable fraction of the $Hg(^3P_1)$ atoms. In view of the fact that hydrogen atoms do not combine with acetylene to any extent[12–14] the most reasonable explanation is that the hydrogen atoms resulting from collisions of molecular hydrogen with $Hg(^3P_1)$ atoms react with ethylene to form ethyl radicals and that these combine to form butane as found by

TABLE II. *Static runs—rates.*

RUN	P_0 mm	ΔP_{obs} mm	ΔT hr.	$\Delta P_{obs}/\Delta T$ mm/hr.	C_2H_2 cc	$\Delta P_{C_2H_2}/\Delta T$ mm/hr.
98	0.19	—	—	0.024	—	—
96	0.28	—	—	0.030	—	—
97	0.55	—	—	0.042	—	—
100	1.01	—	—	0.048	—	—
104	1.24	—	—	0.095	—	—
72	2.8	—	1.0	—	0.49	0.11
71	4.00	0.15	1.25	0.122	0.52	0.11_6
68	6.06	0.17	1.5	0.113	—	—
69	6.12	—	1.5	—	0.76	0.113
67	10.10	0.31	2.5	0.124	1.34	0.120
66	14.67	0.34	3.0	0.113	1.43	0.107
60	27.5	—	8.0	—	2.96	0.083
62	27.5	—	12.0	—	4.00	0.074
73	27.83	0.40	6.0	0.068	2.08	0.077
64	27.9	—	4.1	—	1.42	0.078
70	49.94	0.41_5	9.0	0.046	2.08	0.052
52	71.4	—	7.0	—	0.93	0.030
51	71.88	0.38	14.0	0.027	1.98	0.032
57	72.0	—	22.0	—	3.54	0.034
50	71.99	0.43	17.0	0.025	2.42	0.032
58	200.0	—	4.1	—	0.42_8	0.0094*
59	201.0	—	8.0	—	0.77	0.0087*
61	200.0	—	12.0	—	1.09	0.0082*
54	74.7	—	8.2	—	2.86	—*
56	73.7	—	4.0	—	1.45	—*

* As Flask *F* (Fig. 1) was not large enough to contain the contents of cell S_1 when the pressure was 200 mm another cell, S_2, was used. It was calibrated against S_1 in runs 54 and 56, using 0.032 mm/hr. as the value of $\Delta P_{C_2H_4}/\Delta T$. The rates given for runs 58, 59 and 61 are those which would have obtained if cell S_1 had been used.

[11] E. W. R. Steacie, Can. J. Research **B18**, 44 (1940).

[12] K. F. Bonhoeffer and P. Harteck, Zeits. f. physik. Chemie **139**, 64 (1928).

[13] H. von Wartenberg and G. Schultze, *ibid.* **B2**, 1 (1929).

[14] K. H. Geib and E. W. R. Steacie, *ibid.* **B29**, 215 (1935); Trans. Roy. Soc. Can. **III29**, 91 (1935).

Jungers and Taylor[7] or react with more ethylene to form butyl radicals. In this connection the analysis of the products found in the circulating and single pass runs will be of interest.

The runs illustrated by curves *B* and *C* in Fig. 7 seem to justify the explanation given in the last paragraph. They are all drawn to the same scale but are shifted vertically for convenience. The run shown by curve *B* was stopped after the maximum was passed and all non-condensible gas pumped off. After waiting the usual time for the mercury vapor pressure to attain its equilibrium value the lamp was again turned on and pressure readings taken. The resulting rise in pressure indicates that the presence of the non-condensible gas (hydrogen, as shown subsequently) was responsible for the decrease. In order to show that the second increase is not due to the reaction following a different course at the lower pressure resulting from the removal of the hydrogen, the run illustrated in curve *C* was made. This run was interrupted in the same place as before but this time the gas was pumped down homogeneously to the same pressure as before. When the run was then continued the pressure decreased with approximately the same rate as in curve *A*.

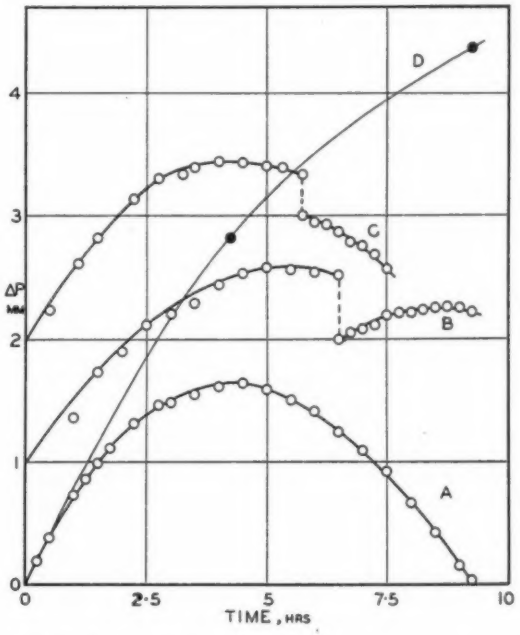

FIG. 7. Effect of hydrogen on the pressure decrease. ○ Observed pressures *vs.* time; ● pressure of acetylene *vs.* time. Static runs.

Circulating runs

These were made largely for the purpose of identifying products. Since the lamp-cell was not thermostated pressure readings taken during a run were not very accurate. Cell temperatures during a run were followed by means of a thermocouple inserted in the thermometer well, *W* (Fig. 2). Figure 8 shows the course of two runs made with an initial ethylene pressure of 70 mm. Curve *A* shows the observed pressure changes with a trap temperature of −117°C. Curve *B* is for the same run with the pressures all corrected back to the original temperature of 25°C. A small initial pressure increase is indicated as in the case of the static runs. Curve *C* shows the observed pressure changes for a run at the same original pressure but with the trap, T_1, at room temperature. The greater rate of pressure decrease shows that the trap is quite efficient in removing the higher boiling products which would lead to subsidiary reactions.

The condensible products from four runs at 210 mm and two runs at 70 mm pressure were added together and distilled in the low temperature still. The only product other than acetylene and ethylene which could be detected was a liquid boiling in the butane-butene range. This was drawn off and analyzed by bromination and found to be 43 percent butene (the particular isomer or isomers were not determined) and 57 percent butane. The remaining liquid, which had a boiling range too high for this still, was fractionated on the high temperature still and found to consist of hexenes and a smaller residue of higher boiling liquid. The quantities are given in Table III.

The non-condensible gas from a 2½-hour run at an initial pressure of 164 mm and a final pressure of 75 mm was analyzed by combustion and found to consist entirely of hydrogen.

Single pass runs

The results of four single pass runs are given in Table IV. These were made with a flow rate of 350 cc per minute (N.T.P.). The pressure in the system was kept at 170 to 180 mm by adjusting the stopcock S_4 (Fig. 2) and higher

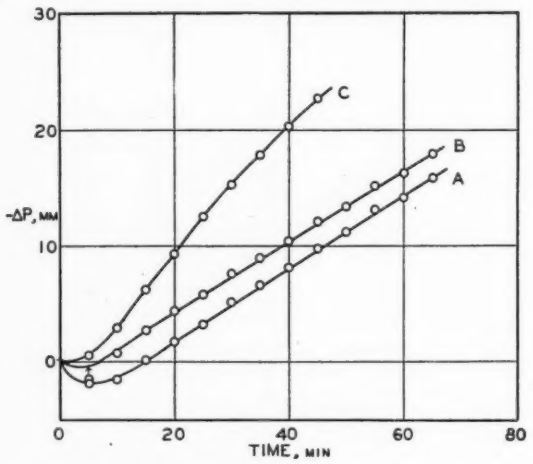

FIG. 8. Pressure decrease *vs.* time for circulating runs. Curve *A*, observed pressure *vs.* time with trap at −117°C; Curve *B*, corrected pressure *vs.* time with trap at −117°C; Curve *C*, observed pressure *vs.* time with trap at room temperature.

liquids were collected in the trap T_1. Under H_2 and C_2H_2 are given the volumes of hydrogen and acetylene produced in cc at 25°C. Under C_4, C_5, and C_6 are given the volumes of the liquid products boiling in the butane-butene, pentene and hexene ranges, respectively. The volume of "pentene" is not considered significant as it was obtained in cutting from the C_4 to the C_6 fraction and probably consists of a mixture of the two. The C_4 fraction was analyzed by the method of Marion and Ledingham[15] and found to be 52 percent butene and 48 percent butane.

Effect of light intensity

Since the effect of light intensity on a photochemical reaction often gives important information about the individual steps in the reaction some runs were made to investigate this factor. The static cell, S_1, was used. By placing a copper gauze screen coated with a layer of copper sulphide between the thermostat window and the cell the light intensity could be cut down to 0.317 times its normal value. The transmission of the screen was determined by means of an FJ-405 photo-cell. A normal run without the screen was made at a pressure of 27.9 mm and the initial rate of production of acetylene was found to be 0.346 cc per hour. A run made at the same pressure but with the screen interposed between the lamp and the cell gave a rate of 0.104 cc per hour against a value of 0.109 calculated on the assumption that the rate is directly proportional to the light intensity. If the rate had varied as the square root of the light intensity the second rate would have been 0.195 cc per hour, so we are quite justified in assuming a linear relation.

Quantum yield

Although a knowledge of the quantum yield is fundamental to the deduction of any mechanism no previous measurements on this quantity have been made. The problem of measuring the quantum yield of a photosensitized reaction is not as simple as that of an ordinary photochemical reaction because of the complications due to quenching and imprisonment of the radiation. This difficulty was largely overcome by using a pressure of 13 mm where the quenching is approximately 100 percent. At this pressure, too, the over-all reaction in the early stages is almost entirely

$$C_2H_4 \rightarrow C_2H_2 + H_2$$

and so the amount of ethylene decomposed is equal to the amount of acetylene produced.

Cell S_1 was used but the window of the thermostat was cut down to a hole one inch in diameter to ensure that all the radiation incident on the cell could also be made to fall on the actinometer. The uranyl oxalate solution used as the actinometer was contained in quartz cells with plane windows. Two different actinometer cells were used, 40 cc and 25 cc.

Brackett and Forbes[16] state that the quantum yield of uranyl oxalate at 253 mμ is 0.63±0.03 at 27±2°C. From an inspection of the spectrum of the lamp the only wave-lengths other than 2537A likely to affect the uranyl oxalate are those at 3126 and 3132 and possibly that at 2967A. Wave-lengths above 3300A were not absorbed by the uranyl oxalate to any extent. In view of this and the fact that about 90 percent of the radiation is concentrated in the resonance line it is reasonable to assume that within the accuracy of the determinations the intensity of

[15] L. Marion and A. E. Ledingham, Ind. Eng. Chem. Anal. Ed. **13**, 269 (1941).

[16] F. P. Brackett and G. S. Forbes, J. Am. Chem. Soc. **55**, 4459 (1933).

2537A can be determined directly by the uranyl oxalate actinometer.

The procedure adopted was to make an ethylene run and determine the rate of production of acetylene. (The relatively short durations of these runs ensured that only acetylene and hydrogen were produced. See, for example, Table II). This was followed by a uranyl oxalate run. Two sets of determinations were made in this way. The average light intensity was 2.62×10^{-5} einstein per hour and the rate of production of acetylene was 0.97×10^{-5} mole per hour giving a quantum yield of 0.37. This value is valid, of course, only for a pressure of 13 mm and for the initial stage of the reaction. Quantum yields for other pressures may be calculated from this and the data of Fig. 6.

Discussion

Comparatively little information is available on the reaction from a quantitative point of view. Olson and Meyers[1,3] stated that on prolonged exposure of ethylene to excited mercury the pressure dropped to about 25 percent of the original, in qualitative agreement with our results (Fig. 1). They found methane and ethane among the products as well as hydrogen and acetylene. Taylor and Bates[2] also found methane in the non-condensible products of the reaction to the extent of 12 percent. In order to explain this Olson and Meyers[3] suggested that the reaction

$$C_2H_4\rightarrow 2CH_2$$

was important. While we found no evidence of methane in our work, it is not unlikely that on prolonged exposure some would be formed as it is a frequent product of reactions which are carried to completion. However, we do not suggest that there is any C−C bond splitting.

Bates and Taylor[4] suggested as a primary step the reaction

$$C_2H_4+Hg(^3P_1)\rightarrow C_2H_2+H_2+Hg(^1S_0), \quad (A)$$

and this has been accepted in principle by us. The polymerization of acetylene was said to be an important second step.

Taylor and Hill[5] stated that under the influence of excited mercury, acetylene, hydrogen and a thick viscous oil were formed and they gave a list of possible reactions subsequent to (A) which would lead to the production of ethane, butene, butane, etc. However they did not have the necessary analytical data available to establish these secondary reactions.

Melville[6] did a few experiments on ethylene in connection with his work on the mercury photosensitized polymerization of acetylene. He confirmed the well-known initial pressure rise but in the absence of analytical data was led to assume that the acetylene polymerized readily and that the polymer was subsequently hydrogenated by hydrogen atoms produced in the reaction

$$H_2+Hg(^3P_1)\rightarrow H+H+Hg(^1S_0).$$

He even assumed that after the maximum in total pressure was reached the hydrogen and acetylene disappeared in equimolecular amounts. It must be emphasized, however, that in his work the only measurements actually made were of the over-all pressure and the pressure of non-condensible gas. His results also showed that the rate of pressure increase increased with increasing pressure but since he only covered the range from 0.063 mm to 9.88 mm, his results are in qualitative agreement with ours. This is shown in curve *A* of Fig. 6 where the rate falls off to zero at the low pressure end because of incomplete quenching.

The more important factors which we have established in our work, and which must be explained by any proposed mechanism, are the following. (1) The initial pressure rise at low pressures corresponds exactly with the amount

Table III. *Circulating runs—liquid products.*

Liquid	Volume
butane-butene	0.6 cc
hexene	0.6 cc
higher	0.2 cc

Table IV. *Single pass runs—products.*

Run	Time min.	H_2 cc	C_2H_2 cc	Liquids			
				C_4	C_5	C_6	Higher
23	65	113	144				
24	30	64	70				
25	300	—	—	0.3 cc	0.05 cc	0.3 cc	0.3 cc
26	460	—	—				

of acetylene and hydrogen produced. (2) Hydrogen is the only non-condensible product. (3) At higher pressures there is evidence that the initial rate of production of acetylene is greater than the rate of pressure increase. (4) Butane and butene are important products of the reaction. (5) Acetylene is relatively inert up to high concentrations. (6) The rate of reaction decreases with increasing pressure. (7) The rate is directly proportional to the light intensity. (8) The quantum yield is less than unity.

The fact that the rate falls off when the pressure is increased above 10 mm suggests that some sort of deactivation process is occurring. This is shown even better by curve *B* of Fig. 6, where the rates are plotted against the reciprocal of the pressure. Although polymerization is probably occurring simultaneously at the high pressure end and incomplete quenching is prominent at the low pressure end, the curve is not inconsistent with a deactivation mechanism.

We are then led to assume a reaction of the type

$$C_2H_4+Hg(^3P_1)\rightarrow C_2H_4^*+Hg(^1S_0), \quad (1)$$

where $C_2H_4^*$ is either an activated ethylene molecule or some mercury-ethylene complex. This is then followed by either

$$C_2H_4^*+C_2H_4\rightarrow 2C_2H_4 \quad (2)$$

or

$$C_2H_4^*\rightarrow C_2H_2+H_2, \quad (3)$$

reaction (2) being more prominent as the pressure is increased. This mechanism is consistent with our value of the quantum yield and largely overcomes the objections[17] which many have held for the reaction

$$C_2H_4+Hg(^3P_1)\rightarrow C_2H_2+H_2+Hg(^1S_0).$$

As an alternative primary process the reaction

$$C_2H_4+Hg(^3P_1)\rightarrow C_2H_3+H+Hg(^1S_0)$$

has been proposed. But while the products of this reaction would doubtless lead to the polymerization of ethylene it is difficult to account for the initial pressure increase by this process.

As mentioned before, butane probably arises from the reactions

$$H_2+Hg(^3P_1)\rightarrow 2H+Hg(^1S_0), \quad (4)$$

$$H+C_2H_4\rightarrow C_2H_5, \quad (5)$$

$$2C_2H_5\rightarrow C_4H_{10}. \quad (6)$$

Evidence that ethyl radicals cause a rapid polymerization of ethylene with a negligible temperature coefficient between 130°C and 245°C[18] suggests that the reactions

$$C_2H_5+C_2H_4\rightarrow C_4H_9 \quad (7)$$

and

$$C_4H_9+C_2H_4\rightarrow C_6H_{13} \quad (8)$$

are important in the production of butene, hexene and higher liquids. This is further substantiated by the work of Burnham and Pease on the inhibition of the thermal polymerization of ethylene by nitric oxide.[19] They found that the time for 20 percent reaction was increased by a factor of three in the presence of 20 mm of nitric oxide and took this as evidence of a free radical mechanism.

Our evidence that at higher pressures the rate of production of acetylene is greater than the rate of pressure increase, while not very convincing, might be taken to suggest that butene is formed by the reaction

$$C_2H_4^*+C_2H_4\rightarrow C_4H_8 \quad (9)$$

as well as by way of reaction (7). However there is little doubt that reaction (7) is of major importance since Pease[20] found a steric factor of 1/2000 for reaction (9). Too much weight must not be given to such a steric factor, however, because of the uncertainty regarding the nature of the primary step of the thermal reaction. If the thermal polymerization is of the radical chain type Pease's value of 35 kcal. for the activation energy may be considerably lower than the activation energy of the primary step. If this is the case the steric factor for the reaction

$$C_2H_4^*+C_2H_4\rightarrow$$

may not be nearly as small as that calculated from Pease's data. Without attempting to

[17] E. W. R. Steacie, Ann. N. Y. Acad. Sci. **41**, 187 (1941); H. S. Taylor, Ann. N. Y. Acad. Sci. **41**, 200, 202 (1941).

[18] J. C. Jungers and L. M. Yeddanapalli, Trans. Faraday Soc. **36**, 483 (1940).

[19] H. D. Burnham and R. N. Pease, J. Am. Chem. Soc. **62**, 453 (1940).

[20] R. N. Pease, J. Am. Chem. Soc. **53**, 613 (1931).

criticize the accuracy of his work we must also consider the results of Storch[21] and of Krauze, Nemtzov and Soskina[22] whose results lead to considerably greater collision efficiencies.

Even assuming the value 1/2000 to be the correct collision efficiency for the thermal polymerization of ethylene the validity of applying this to reaction (9) is questionable because of the uncertainty regarding the nature of thermal *vs.* photosensitized activation. One thing is certain, however, and that is that reaction (9) is much less important than either (2) or (3).

In view of the importance which we have attached to activated ethylene molecules it is of interest to calculate their lifetime. Our mechanism for the early stages at low pressure is

$$C_2H_4+Hg^*\rightarrow C_2H_4^*+Hg, \qquad (1)$$

$$C_2H_4^*+C_2H_4\rightarrow 2C_2H_4, \qquad (2)$$

$$C_2H_4^*\rightarrow C_2H_2+H_2. \qquad (3)$$

For the steady state

$$0=d/dt[C_2H_4^*]=k_1[Hg^*][C_2H_4]-k_2[C_2H_4^*][C_2H_4]-k_3[C_2H_4^*]$$

or

$$[C_2H_4^*]=\frac{k_1[Hg^*][C_2H_4]}{k_3+k_2[C_2H_4]}.$$

The rate of production of acetylene is given by

$$R_3=k_3[C_2H_4^*].$$

Substituting for $[C_2H_4^*]$ we get

$$1/R_3=\frac{1}{k_1[Hg^*]}\cdot\frac{1}{[C_2H_4]}+\frac{k_2}{k_3k_1[Hg^*]}.$$

That is to say a plot of $1/R_3$ *vs.* $1/[C_2H_4]$ should give a straight line for which the ratio of the intercept on the $1/R_3$ axis to the slope is k_2/k_3. k_3 is the reciprocal of the lifetime τ_3 of an activated ethylene molecule. Assuming tentatively that the steric factor for reaction (2) is unity, $k_2=A_2\sigma_2^2$. If $[C_2H_4]$ is measured in mm the value of A_2 for 25°C is 2.18×10^{21}. By using the kinetic theory value of 5.56×10^{-8} cm for the diameter of the ethylene molecule $k_2=6.74\times10^6$. From the data of Table II for the range 0.19 mm to 4.0 mm the ratio of the intercept to the slope on the $1/R_3$ *vs.* $1/P_0$ curve is 1.4. τ_3 is then approximately 2×10^{-7} sec. A steric factor less than unity for reaction (2) would of course increase this value, but in any case a lifetime of 10^{-6} to 10^{-7} second does not seem unreasonable for an activated ethylene molecule.

One of the most unexpected results which we have obtained has to do with the production of acetylene. As mentioned in the Introduction previous workers have assumed that acetylene will polymerize readily in the presence of ethylene. Our results, as shown in curve *D* of Fig. 7, are in sharp disagreement with this, acetylene concentrations of over 30 percent being obtained in several cases. This suggests that acetylene either has a small quenching cross section for $Hg(^3P_1)$ atoms or that it, too, polymerizes by an activated molecule process. A few runs were made on a 20 percent mixture of acetylene in ethylene using $Cd(^3P_1)$ atoms. The quantum yield for the reaction between $Cd(^3P_1)$ atoms and ethylene is very small[23] but pure acetylene was found to react very readily. However the rate with the 20 percent mixture was about 1/20 to 1/30 of that with pure acetylene, showing that in this case, too, acetylene is relatively inert. The investigation of quenching cross sections now going on in this laboratory is expected to clarify the problem considerably.

In conclusion the authors wish to express their indebtedness to Dr. Léo Marion and Mr. A. E. Ledingham for making the microanalyses of the butane-butene mixtures.

[21] H. H. Storch, J. Am. Chem. Soc. **56**, 374 (1934).

[22] M. V. Krauze, M. S. Nemtzov and E. A. Soskina, Comptes rendus Acad. Sci. U.R.S.S. **2**, 301 (1934); J. Gen. Chem. (U.S.S.R.) **5**, 343 (1935).

[23] E. W. R. Steacie and R. Potvin, Can. J. Research **B18**, 47 (1940).

Further Studies on the Oxidation of Nitric Oxide; the Rate of the Reaction between Carbon Monoxide and Nitrogen Dioxide*

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The initial rate of the reaction between CO and NO_2 from 225°C to 290°C was measured under conditions which precluded the possibility of NO_2 decomposition. This study extends the earlier data on the reaction over a 300° temperature interval. The oxidation of nitric oxide at 25°C and at pressures from 0.01 to 0.1 mm of NO was found to be third order over a 3- and 6-fold change in reactants. The CO_2 and NO_2 production in systems containing NO, CO, and O_2 around 150°C was measured under conditions in which the formation of CO_2 by the reaction between CO and NO_2 was negligible. It is concluded that NO_3 is the intermediate needed to correlate this and previous data on reactions involving NO and NO_2, and that the rate of the reaction of NO_3 with NO is faster than that with CO.

A new apparatus containing greaseless valves capable of handling quantities of products of the order of 10^{-3} mm, and a method of analysis precise to 3×10^{-5} mm was devised. Methods to prepare reactant gases of the requisite purity are described.

THE complex of reactions in the system containing nitric oxide, nitrogen dioxide, and oxygen, together with carbon monoxide or hydrogen has been studied at high temperatures in previous investigations.[1] By selection of proper conditions the rate constant for the reaction of carbon monoxide and nitrogen dioxide was obtained. In the attempt to set conditions so that the rate determining step in the sequence

$$2NO+O_2\rightarrow 2NO_2, \qquad (1_B)$$

$$NO_2+CO\rightarrow CO_2+NO \qquad (3)$$

would be (1_B), the classical termolecular oxidation of nitric oxide, it was found that the rate was first order for nitric oxide. The specific rate was about the same with hydrogen in place of carbon monoxide. To explain this first order effect of nitric oxide, the intermediate formation of NO_3 was assumed. Such a process would lend support to the hypothesis that this intermediate is involved in the mechanism of the termolecular oxidation of nitric oxide studied by Bodenstein and others.[2] Following previous suggestions[3] the present investigation represents a study of the system at low temperatures where the decomposition of nitrogen dioxide and its reaction with carbon monoxide are unimportant so that relative rate measurements of the reactions of NO_3 with carbon monoxide and nitric oxide are possible. The work involves (a) a determination of the rate of the reaction of NO_2 and CO from 225.2°C to 290.2°C, (b) a study of the ordinary oxidation of nitric oxide at 25°C, and (c) a measurement of the production of CO_2 and NO_2 in a system made up of NO, O_2 and CO.

Experimental

Apparatus

The apparatus similar to that previously described consisted of a 150 ml glass reaction cell maintained at a constant temperature by a mercury liquid-vapor thermostat.[4] Pressures of oxygen and carbon monoxide were measured by mercury manometers connected to the system by traps cooled with solid carbon dioxide.

A new greaseless high vacuum valve[5] inert to corrosive gases was developed to remove the difficulty caused by the reaction of nitrogen dioxide with stopcock grease. This valve consisted of a corrugated noble metal diaphragm covered with a thin film of silver chloride which served as the valve seat, and a two-millimeter

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[1] See R. H. Crist and J. E. Wertz, J. Chem. Phys. **7**, 87 (1939) for the references of this investigation.

[2] For references to the older literature see Kassel, *Kinetics of Homogeneous Gas Reactions* (Chemical Catalog Company, 1932), p. 165.

[3] R. H. Crist, J. Chem. Phys. **7**, 90 (1939).

[4] Rittenberg and Urey, J. Am. Chem. Soc. **56**, 1885 (1934).

[5] Brown and Crist, Ind. Eng. Chem. Anal. Ed. **11**, 396 (1939).

glass capillary with a polished convex surface that fitted the seat to provide closure. A precision of 3×10^{-5} millimeter was possible in a system equipped with these valves.[6]

A Pirani-Hale gauge having a volume of 25.9 ml and a length of 30 cm was used to measure the pressure of carbon dioxide and the nitrogen oxides. The Pyrex capillary filament filled with mercury had a length of 40 cm and a resistance of 200 ohms. In operation, the outer wall of the cell was maintained at the ice point. The current passing through the filament was maintained constant, and the voltage decreased with an increase in pressure. Consequently, the calibration of the pressure gauge was made by determining $(E_{vac}-E_p)$ for known pressures of nitric oxide and carbon dioxide measured on a McLeod gauge. At random points the nitric oxide was converted into nitrogen dioxide to check the calibration for nitrogen dioxide. At low pressures, the value of $(E_{vac}-E_p)$ as measured on a Type K potentiometer varied by 1.6 millivolts per 1×10^{-3} mm change in pressure, giving a precision of 0.03×10^{-3} mm in the pressure, when appropriate volume ratios were used.

Preparation of materials

The carbon monoxide was prepared from formic acid. A preliminary purification was effected by passing the gas slowly through four wash columns containing, respectively, 20 percent potassium hydroxide solution, 10 percent potassium hydrosulfite solution, potassium hydroxide solution, and 95 percent sulfuric acid. The gas was then condensed in a trap by liquid nitrogen. Samples from a middle liquid fraction of this reacted at room temperature with nitrogen dioxide to produce condensable products other than carbon dioxide and nitric oxide. A more vigorous purification was effected by heating at 250°C for 2 hours with 0.1 millimeter of nitrogen dioxide. This carbon monoxide after passing through a liquid nitrogen trap contained less than one part per million of condensable material and on standing at room temperature with either oxygen or nitrogen dioxide produced but one part in ten million of carbon dioxide. Nitric oxide was present to the extent of four parts in ten thousand. For some of the experiments this was reduced to four parts per million by adding excess nitrogen dioxide and freezing out as N_2O_4.

Nitrogen dioxide was prepared by heating lead nitrate and other oxides of nitrogen were removed from the sample by pumping at −100°C until the pressure when measured at −120°C was less than 10^{-4} mm. It was stored in the dark as the solid by liquid nitrogen. No change was noted over a period of three months.[7]

The oxygen was prepared from potassium chlorate which was thoroughly outgassed during initial decomposition. The sample for use was first passed through a tube containing finely divided silver crystals at 600°C to remove any chlorine present, then through a coil immersed in liquid nitrogen, and finally condensed in a trap with solid nitrogen. Oxygen prepared in this way contained four parts per million of condensable material. One hundred millimeters of the gas mixed with 0.089 mm of NO at 265°C produced in 45 minutes only 0.36 part per million of material which was analyzed as carbon dioxide.

The nitric oxide was prepared by the reduction of nitrate ion by iodide ion according to the method described by Johnston and Giauque.[8] After fractional distillation, a sample contained one part in ten thousand of material which was condensed at −195°C. This condensate which was a gas between −150 and 160°C was removed by subliming the nitric oxide between the temperatures of −195°C and −210°C, the vapor pressures of nitric oxide being 0.08 and 1×10^{-4} mm, respectively. The lower temperature was obtained by keeping the pressure in a liquid nitrogen Dewar flask at 85 mm with a barostat arrangement.

The carbon dioxide used for the calibration of the Pirani gauge was the sublimate at −140°C from a sample prepared by heating calcite.

[6] This precision was not possible with the available valves and stopcocks, the first experiments on the oxidation of carbon monoxide by nitrogen dioxide having shown that ordinary stopcocks could not be used. Stopcock grease in contact with NO_2 was oxidized to products which were gaseous at 150°C and froze out with liquid nitrogen. The quantity varied from 10^{-3} to 10^{-2} mm per hour, it being dependent on the lighting and the length of time that the grease had been in the system. All the hydrocarbon lubricants tried were shown to form carbon dioxide in the presence of nitrogen dioxide at room temperature.

[7] It was found that decomposition always resulted when solid NO_2 at −80°C was stored with P_2O_5.

[8] Johnston and Giauque, J. Am. Chem. Soc. **51**, 3194 (1929).

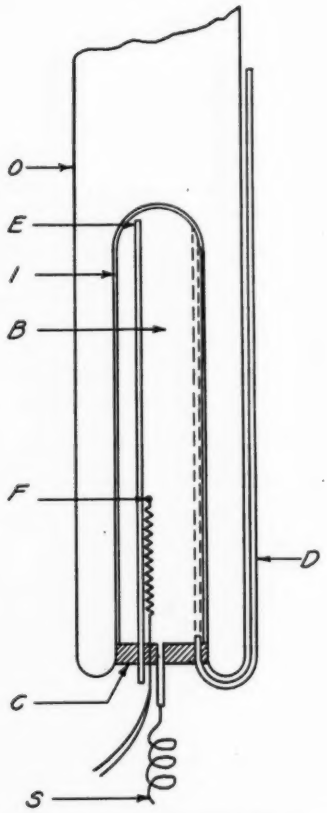

FIG. 1. Low temperature distillation apparatus. *O*—outer glass wall of 18-mm Pyrex tubing; *I*—inner glass wall of 12-mm Pyrex tubing. This surface is maintained at a constant temperature by the copper block which touches its inner surface; *B*—copper block closely fitting into *I*. The temperature of this block is controlled by immersing the projection on its lower end in liquid nitrogen. *F*—thermocouple soldered to *B*. This was calibrated at −196°C and −79°C. It was also checked against the vapor pressure of carbon dioxide measured on a McLeod gauge; *C*—supporting cork; *D*—ethyl bromide addition tube. The purpose served by the ethyl bromide was to provide better contact between the glass and the copper; *E*—air vent and overflow; *S*—Nichrome wire spiral (*B.* & *S.* No. 36) soldered on the projection from the copper block.

All gases were stored in Pyrex containers behind silver chloride valves.

Methods of analysis

The separation and identification of carbon dioxide and the several oxides of nitrogen were based on their respective vapor pressure temperature relations. In the separations the temperature was controlled by means of the apparatus shown in Fig. 1. The particular design is adapted to the handling of small amounts of material with a minimum of liquid nitrogen. In operation, the ethyl bromide (see the figure) was added through *D*, the copper tip immersed in liquid nitrogen, and when the required temperature was reached, the level of the liquid nitrogen was lowered along the Nichrome wire spiral until the heat conducted through the analysis tube was just balanced by that passing down the spiral to the liquid nitrogen. Under these conditions the temperature was constant to ±2°C for half-hour periods.

The procedure used when analyzing for carbon dioxide only was based upon its sublimation from a mixture with the condensed oxides of nitrogen. The sample was held at −150°C where the pressure of carbon dioxide is 6×10^{-2} mm, while that of NO_2 and N_2O_3 is less than 10^{-5} mm. The evaporating carbon dioxide was condensed by liquid nitrogen in a side tube on the Pirani gauge where its pressure at 0°C was measured. Identification of the sample of gas as carbon dioxide was made frequently by determining its vapor pressure curve. In these determinations, the analysis apparatus was used for control of the temperature in the same way that it was in the original tests of the vapor pressures of carbon dioxide. The validity of the method is shown in Table I which contains the data on three representative samples.

Sample I shows the reliability of the carbon dioxide separation from nitrogen dioxide and also demonstrates the additivity of their pressures measured on the Pirani. (See columns 2, 3, and 6.) Sample II shows the separation of carbon dioxide from mixtures containing nitric oxide, nitrogen dioxide and carbon dioxide. The recovery of carbon dioxide from a sample con-

TABLE I. *The analysis of carbon dioxide.*

	Composition of Sample in mm of Hg×10²					Material Recovered		
Sample	CO_2	NO_2	NO	CO	Total exp.	NO_2	CO_2	Error in CO_2 Analysis
I	2.09	3.60	0	0	5.68	3.25	2.06	−1.4%
II	2.21	3.80	22.9	0			2.15	−2.8%
III	2.83	3.05		200 (mm)			2.77	−2.2%

TABLE II. *Analysis for carbon dioxide and nitric oxide.*

	Composition of the Sample in mm of Hg				Found by Analysis	
	CO	NO	NO_2	O_2	NO	CO_2
I	0	0.0350	0	5.0	0.0352	
II	0	0	0.0049	0	0.0002	0
III	0	0.0264	0.0177	5.0	0.0270	
IV	98	0.0140	0.0140	7.5	0.0137	0.0001

TABLE III. *Reaction of carbon monoxide and nitrogen dioxide.*

TEMP. IN °C	NO_2 IN (MM Hg)	CO IN (MM Hg)	CO_2 IN MM Hg$\times 10^3$	FRACTION OF NO_2 REACTING	TIME IN SEC.$\times 10^{-3}$	k_3 CC MOLE^{-1} SEC.$^{-1}$	AVERAGE
225.2	0.2779	285.0	5.71	0.02	7.20	0.313	
225.2	0.535	220.6	8.54	0.02	7.38	0.306	
225.2	0.549	136.2	6.23	0.01	8.22	0.317	0.312±0.004
237.1	0.413	105.0	10.48	0.03	12.66	0.600	
237.2	0.172	101.7	4.18	0.03	10.02	0.751	0.675±0.075
249.5	0.289	139.0	5.58	0.02	3.60	1.25	
249.5	0.284	141.0	5.72	0.02	3.66	1.27	
249.5	0.285	140.5	11.00	0.04	7.32	1.22	
249.5	0.271	141.8	15.16	0.06	10.86	1.18	
249.5	0.538	140.0	10.34	0.02	3.72	1.19	
249.5	0.560	140.7	21.61	0.04	7.44	1.19	
249.5	0.565	140.8	30.30	0.06	10.68	1.16	
249.5	0.277	285.7	29.49	0.10	10.80	1.12	
249.5	0.278	287.5	21.70	0.08	7.38	1.20	1.20 ±0.03
263.0	0.0521	187.2	3.22	0.06	3.60	3.07	
263.0	0.0518	100.0	1.77	0.03	3.69	3.10	
263.0	0.0590	100.0	3.91	0.07	7.20	3.08	3.08 ±0.01
290.1	0.0668	32.6	4.41	0.07	4.47	14.9	
290.1	0.0500	77.9	2.63	0.05	1.68	14.1	
290.1	0.1060	40.6	4.73	0.05	2.58	15.0	
290.1	0.1515	56.1	10.49	0.07	3.84	11.3	13.8 ±1.2
290.2	0.1351	44.7	4.61	0.04	1.77	15.1	
290.2	0.0688	84.9	5.07	0.07	2.58	11.8	
290.2	0.0553	125.3	4.51	0.08	1.98	11.5	
290.2	0.1260	39.8	3.31	0.03	1.62	14.3	13.2 ±1.1

taining carbon monoxide, nitrogen dioxide and carbon dioxide is illustrated by sample III.

The determination of nitrogen dioxide in the presence of nitric oxide with oxygen absent was made by adding an excess of the NO to the sample, freezing down the nitrogen dioxide as N_2O_3 at 160°C and pumping off the uncondensed nitric oxide. The pressure of the residue was measured and from this the nitrogen dioxide was calculated. A known sample containing 5.60×10^{-2} mm of nitrogen dioxide which was carried through these operations showed a recovery of 5.75×10^{-2} mm representing a 3 percent error. This was the largest deviation of the known samples handled in this way.[9]

The determination of both nitric oxide and nitrogen dioxide with oxygen present could not be made by methods previously described because of the increased rate of oxidation of nitric oxide at low temperatures used for the separations. Analysis here depended upon the quantitative removal of nitrogen dioxide by liquid mercury.[10] The sample was divided into two parts, one for the determination of carbon dioxide by the method outlined, and the other for the determination of nitric oxide. After the latter fraction was agitated with mercury by moving a mercury column up and down for five minutes, the remaining gas which contained nitric oxide and oxygen was pumped slowly through two traps in liquid nitrogen to obtain complete oxidation of the nitric oxide. The pressure of this NO_2 was a measure of the NO in the original sample, and by difference gave the amount lost in the primary reaction under consideration. Some data to show the reliability of the method are given in Table II. The samples illustrate the analysis as follows: I shows the conversion of NO to NO_2 in the two traps, II the removal of NO_2 by mercury,

[9] It is interesting to note that a mixture of NO and NO_2 may also be separated by repeated cycles of freezing, pumping and evaporating the sample. Eight cycles performed in this way over a period of eight hours effected a separation of the oxides. The sample contained originally 0.029 and 0.124 mm of NO_2 and NO, respectively, giving a measured total pressure of 0.152 mm. The total pressures for the freezing cycles 1, 2, 4 and 8 were 0.047, 0.033, 0.033, 0.031 and 0.0305 mm, respectively, showing that 5 percent of the sample remaining was presumably nitric oxide.

[10] See in this connection, W. A. Noyes, Jr., J. Chem. Phys. 5, 807 (1937).

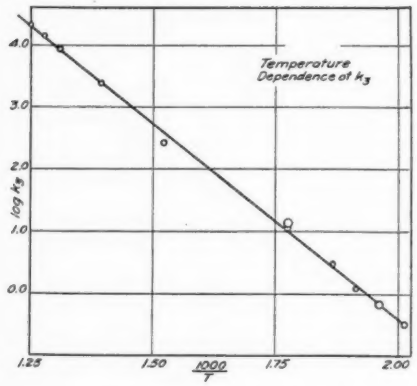

FIG. 2.

III the separation of NO from NO_2, and IV the analysis of a mixture containing a high pressure of carbon monoxide.

RESULTS

Reaction of carbon monoxide and nitrogen dioxide

The reaction of nitrogen dioxide and carbon monoxide was studied in Pyrex glass reaction vessels which were rinsed with potassium chloride solution (1).[11] In order to avoid decomposition of nitrogen dioxide, its pressure had to be low, and the time of reaction short. For these reasons, it was necessary to employ high concentrations of carbon monoxide in order that the reaction would proceed at a measurable rate. Even under these conditions very little carbon dioxide was formed. Since the total change was small, the following form of the rate equation was more appropriate for the determination of the rate constant

$$-\Delta NO_2/\Delta t = +\Delta CO_2/\Delta t = k_3(CO)(NO_2).$$

The data for this study are given in Table III. The temperature range was from 225.2°C to 290.2°C. The nitrogen dioxide and carbon monoxide, and carbon dioxide pressures varied some three fold in the various experiments. The constants calculated from the above equation which are given in the last column, clearly indicate the bimolecular nature of the reaction. The larger average deviation of a single observation found at the highest temperature occurs as the result of the shorter time that must be used to avoid appreciable decomposition of the nitrogen dioxide. The k_3 value at 290.2°C is the least reliable of the four temperatures studied because of the fact that the removal of the sample from the cell required from three to five minutes, which introduces a 10–15 percent error into these half-hour runs.

In order to check on possible heterogeneous reactions several runs were made with a doubled surface volume ratio. The last four runs were made in this cell and showed no wall effect within the experimental error.

The data for the effect of temperature on the rate given in Table III are shown in the plot of Fig. 2 from which an activation energy of 27.8 kcal. per mole is calculated.

The oxidation of nitric oxide at room temperature

It seemed desirable to determine the rate of oxidation of nitric oxide by oxygen at the low pressures used in the later investigation. The pressures used by Bodenstein were around 10 mm for both oxygen and nitric oxide. In Table IV are given the data for the pressure regions of 0.1 to 0.02 mm for nitric oxide and 10 mm for oxygen. The termolecular constant for the reaction (1_B) is given in the last column. The average value of $7.45\pm0.22\times10^9$ cc^2 mole^{-2} sec.$^{-1}$ is to be compared with 7.06×10^9 which is Bodenstein's value at 30°C. The present results vary from Bodenstein's by 5.5 percent. The results vary among themselves by 3 percent. It is noted that the pressures of nitric oxide and oxygen varied four fold among these runs, as compared to a factor of two in Bodenstein's investigation. In addition to establishing the rate of this reaction in a much lower pressure range than that previously studied, the data serve as a check on the analysis method for the oxides of nitrogen in the presence of oxygen.

TABLE IV. *The oxidation of nitric oxide at 25°C.*

	Time Sec.$\times10^{-3}$	O_2 in mm Hg	Initial NO mm Hg	Final NO mm Hg	$k_{1_B}\times10^{-9}$ cc^2 Mole.$^{-2}$ Sec.$^{-1}$
I	24.3	8.2	0.109	0.0555	7.65
II	32.7	7.9	0.060	0.0359	6.84
III	62.4	8.8	0.043	0.0210	7.39
IV	132.0	10.6	0.0203	0.0089	7.80
V	10.2	21.9	0.127	0.0174	7.55
					Average 7.45±0.22

[11] Calhoun and Crist, J. Chem. Phys. **5**, 301 (1937).

TABLE V. *Reaction in* CO, O_2 *and* NO *mixtures.*

TEMPERATURES IN °C	NO IN MM Hg ×10³	O_2 IN MM Hg	CO IN MM Hg	TIME IN SEC. ×10⁻³	CO_2 IN MM Hg ×10³	NO_2 IN MM Hg ×10³	NO_2 CORR. MM Hg×10³	NO_2 CALC. MM Hg×10³	k'×10³
25	35.8±.05	7.5	98	.8	.24±.07	1.8±0.5	1.6±1.0	2.3	7.6
25	51.0±.05	4.2	96	63.3	1.06±.07	14.2±0.5	13.1±1.0	18.5	6.1
25	61.0±.05	6.0	196	79.3	1.81±.07	34.8±0.5	33.0±1.0	33.3	3.4
188	70.0±.06	23.0	162	7.2	3.51±.09	6.7±0.6	3.2±1.2	6.4	47.2
188	89.0±.07	9.5	106	10.9	3.52±.09	9.6±0.7	6.0±1.4	6.4	99.8
180	71.0±.06	9.5	103	86.0	10.00±.07			22.5	61.3
178	82.0±.07	12.5	113	7.2	1.06±.07			4.7	32.8
265	82.5±.07	35.0	97	1.50	1.54±.09			2.0	130.0

Reactions in nitric oxide, oxygen, and carbon monoxide mixtures

Preliminary results showed that significant amounts of carbon dioxide were produced in the temperature range where the nitrogen dioxide present could not account for its formation. The data in Table V were obtained from 25 to 265°C and cover a twofold pressure range of the reactants. In columns 6 and 7 are given the CO_2 and NO_2 obtained in the analyses. If the CO_2 is produced by $CO+NO_3 \rightarrow NO_2+CO_2$ then in order to obtain the NO_2 produced by direct oxidation an amount equal to the CO_2 must be subtracted from the NO_2 by analysis. This is the value given in column 8 as NO_2 (Corr.) while that in column 9 is calculated from the Bodenstein constant. The k' in the last column is obtained from the equation

$$k' = \frac{k_{2a}}{k_2} = \frac{[NO]}{[CO]} \cdot \frac{\Delta[CO_2]}{\frac{1}{2}\Delta[NO_2]}.$$

This equation is derived from $\Delta CO_2/\Delta t = k_{2a}[NO_3][CO]$ and a similar one for the reaction $NO_3+NO \rightarrow 2NO_2$, (see the discussion for the assembly of reactions) where ΔCO_2 and ΔNO_2 are the values from columns (6) and (8), respectively. Under NO_2 (calc.) is given the amount predicted from the Bodenstein rate constant. The best agreement is in the third run at 25°C. This is to be expected as the CO_2 is low and the NO_2 large. It should be noted that the NO_2 is obtained by a difference and the error will become larger the smaller the amount of NO_2 produced. The two runs at 188°C are anomalous. In view of the above discussion the second one is somewhat too good, while the first is much too bad and must carry some accidental error. The three runs recorded in the bottom of the table were the first ones performed and no analysis for NO_2 was made. However, it seems reasonable as a first approximation to use the NO_2 (Calc.) for the calculations of k' for which values are given in the last column. The results are within the precision of the measuring system. The relation of k' with temperature shown in the usual way in Fig. 3 will be useful in the discussion.

DISCUSSION

The reaction of carbon monoxide and nitrogen dioxide

The results of our direct measurement of the reaction of carbon monoxide and nitrogen dioxide have been combined with those of Calhoun and Crist as shown in the plot of log k against $1/T$ given in Fig. 2. The point farthest from the line, namely, that at 385°C is the least reliable of the older data.[12] When less weight is attached to these points, their deviation from the straight line through the remainder is not serious.

The activation energy calculated from the slope is 27.8 kcal., and the rate over the 300 degree range is given by $k = 4.8\times10^{11}(\exp -27{,}800/RT)$. The rate of this reaction has been found, therefore, to be sufficiently low that no correction for it is necessary in the experiments on CO, O_2, NO, and NO_2 mixtures between 25° and 256°C.

[12] If the two sets of data are analyzed independently the best values for the activation energies are 31 and 32.2 kcal., respectively, for the upper and lower groups. When considered as a whole the points at 290 and 385°C are somewhat out of line. It is for these points that the experimental error is the greatest, the time being short at 290°C and the pressure change quite small at 385°C.

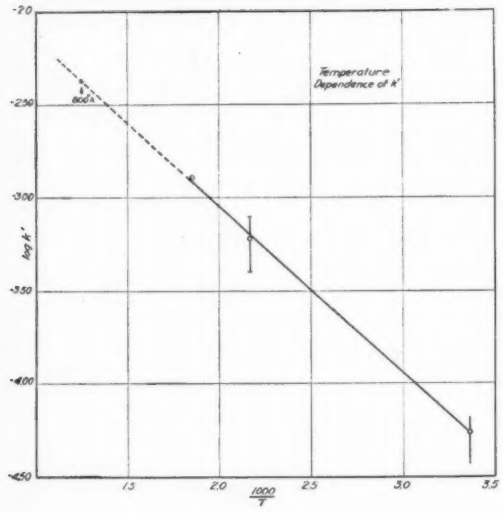

FIG. 3.

The mechanism of the oxidation of nitric oxide

The following equations will be referred to in this discussion:

$$NO+O_2 \rightarrow NO_3, \quad (1)$$

$$NO_3 \rightarrow NO+O_2, \quad (1a)$$

$$NO_3+NO \rightarrow 2NO_2, \quad (2)$$

$$NO_3+CO \rightarrow NO_2+CO_2, \quad (2a)$$

$$NO_2+CO \rightarrow NO+CO_2, \quad (3)$$

$$2NO+O_2 \rightarrow 2NO_2, \quad (1_B)$$

$$NO_2+NO_2 \rightarrow 2NO+O_2. \quad (4)$$

In the work of Calhoun and Crist it was assumed that reaction (1) was followed by (2a), the former being rate determining, and that (2a) was much faster than (2). We can now estimate the relative rates of (2a) and (2) from the data on k' from 250–263°C. To extrapolate to 527°C we use the usual Arrhenius form, namely,

$$\log k' = \log \frac{k_{2a}}{k_2} = \frac{E_2 - E_{2a}}{2.3RT} + \text{constant},$$

where E_2 and E_{2a} are the respective activation energies. The plot of $\log k'$ against $1/T$ is shown in Fig. 3. An extrapolation gives k' at 527°C as 3.2×10^{-3}, and with CO, NO, and O_2 as 600, 25, and 10 mm, respectively, we obtain

$$\frac{-(\Delta CO)_{2a}}{(\Delta NO)_2} = 0.1,$$

a result contrary to the assumption and reaction (2) must remain in the general reaction scheme.

The re-formation of NO_2 by (3) relative to (4) can be estimated at 385°C. Here $k_3 = 2.5\times10^2$ (C and C); k_4[13] $= 5\times10^3$ (Bodenstein and Ramstetter); CO = 600 mm; NO_2 = 8 mm (this being the equilibrium value represents a maximum), and we obtain

$$k'' = \frac{k_4}{k_3[CO]}[NO_2] = 0.3.$$

Actually NO_2 must be considerably below the equilibrium value giving still greater favor to reaction (3).

At the highest temperature of 527°C we can expect k'' to be lower due to a difference in activation energies. Bodenstein and Ramstetter give 26.5 kcal. for (4) and that for (3) is to be taken as either 32.2 of the previous work or the 28 kcal. reported here. It seems reasonable then that k'' would be low enough that the CO pressure could be reduced to one-half its value without affecting the rate, as was observed in the experiment. (See reference 10, p. 305.)

CONCLUSION

If (1_B) were the mechanism of the formation of nitrogen dioxide, this with (3) should represent the high temperature experiments of Calhoun and Crist. In fact, the rate of formation of CO_2 is about what would be expected, but as pointed out the order for NO is not that given by Bodenstein. An examination of his data shows that at 385°C the backward reaction is predominating, and further his variation of initial pressures for establishing the order is rather limited. In view of this the reaction could well be represented by (1) and (2) with (2a) added for the carbon monoxide experiments. This set of reactions is also necessary to explain the production of CO_2 at 200°C where its formation by (3) is unimportant. This would show that the ordinary termolecular oxidation goes in part at least by the NO_3 intermediate mechanism.

[13] The value of k_4 given by Bodenstein and Ramstetter at their highest temperature is probably too large. Hence, both the activation energy of 26.5 kcal. and k'' would be lower. This would lend still greater favor to (3) as compared to (4) for the regeneration of NO.

The Near Infra-Red Spectra of Linear Y_2X_2 Molecules

Part I. Theory

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Complete expressions for the rotation-vibration energies of the linear Y_2X_2 molecules, through second order of approximation, have been obtained in the form $E=hc(G_V+F_R)$. The vibrational term G_V obtained agrees exactly with that found by Wu and Kiang, but there are numerous points of difference in the rotational term F_R.

1. INTRODUCTION

THE linear Y−X−X−Y molecular model is of interest in connection with such molecules as C_2H_2, C_2D_2, C_2Cl_2, etc. It is the purpose of this paper to give, through second order of approximation, a complete treatment of the rotation-vibration energies of the Y_2X_2 molecular model.

The normal vibrations and expressions for the normal frequencies have been studied by Mecke,[1] Dennison,[2] Colby,[3] and Wu and Kiang.[4] The effect of the anharmonicities on the vibration has been investigated by Wu and Kiang.[4] A treatment of the interaction between rotation and vibration has been given by Sayvetz[5] and Wu.[6] It appears that Wu has neglected to consider certain terms in the rotation-vibration Hamiltonian, and his energy expressions are therefore not quite correct. In the light of these errors and as a preliminary to the interpretation of some new experimental work in progress on the band fine-structure of C_2H_2 and C_2D_2 it seemed advisable to recalculate the energy expressions, particularly those involving the interaction between rotation and vibration.

2. THE VIBRATION PROBLEM

The model assumed for the Y_2X_2 type of molecule has, in its equilibrium configuration, the form shown in Fig. 1. A Y particle has mass m and an X particle has mass M. In order to describe the positions of the particles a body-fixed rectangular xyz coordinate system is adopted whose origin lies at the center of gravity of the molecule in its equilibrium state. For reference purposes the particles are numbered as shown in Fig. 1 and the instantaneous position of the ith particle is given by $(x_i, y_i, z_i) = (x_i^0+x_i', y_i^0+y_i', z_i^0+z_i')$ where the primed quantities denote components of displacement from the equilibrium position.

The appropriate body-fixed coordinate system for studying the interactions between rotation and vibration is defined according to the Eckart conditions:[7,8] (a) the origin of coordinates remains at the center of gravity of the molecule and (b) the angular momentum of vibration vanishes in zero approximation. From an inspection of the six equations satisfying the Eckart conditions and the expressions for the relative displacements of the particles in infinitesimal

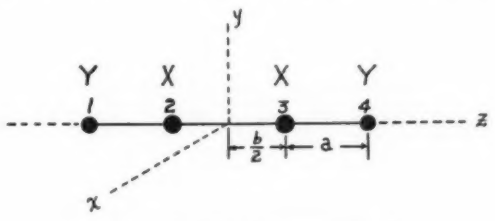

FIG. 1. Equilibrium coordinates.

[1] R. Mecke, Zeits. f. Physik **64**, 173 (1930).
[2] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).
[3] W. F. Colby, Phys. Rev. **47**, 388 (1935).
[4] Ta-You Wu and A. T. Kiang, J. Chem. Phys. **7**, 178 (1939).
[5] A. Sayvetz, J. Chem. Phys. **7**, 383 (1939).
[6] Ta-You Wu, J. Chem. Phys. **8**, 489 (1940).
[7] C. Eckart, Phys. Rev. **47**, 552 (1935).
[8] E. B. Wilson and J. B. Howard, J. Chem. Phys. **4**, 260 (1936).

vibrations, one can readily see that the following intermediate coordinates are suitable ones for this problem:

$$\begin{aligned}
&x=(\tfrac{1}{2})[x_1+x_4-x_2-x_3],\\
&y=(\tfrac{1}{2})[y_1+y_4-y_2-y_3],\\
&\xi=(\tfrac{1}{2})(a+b)^{-1}\{b(x_1-x_4)-(2a+b)(x_2-x_3)\},\\
&\eta=(\tfrac{1}{2})(a+b)^{-1}\{b(y_1-y_4)-(2a+b)(y_2-y_3)\},\\
&z=(\tfrac{1}{2})[z_1+z_4-z_2-z_3],\\
&q=2^{-\frac{1}{2}}(z_1-z_4),\quad \zeta=2^{-\frac{1}{2}}(z_3-z_2).
\end{aligned}\tag{1}$$

The instantaneous coordinates (x_i, y_i, z_i) of the particles can be obtained from the following set of equations:

$$\begin{aligned}
&x_1+x_4=(\mu_1/m)x,\\
&x_1-x_4=(\mu_2/m)[b/(a+b)]\xi,\\
&x_2+x_3=-(\mu_1/M)x,\\
&x_2-x_3=-(\mu_2/M)[(2a+b)/(a+b)]\xi,\\
&y_1+y_4=(\mu_1/m)y,\\
&y_1-y_4=(\mu_2/m)[b/(a+b)]\eta,\\
&y_2+y_3=-(\mu_1/M)y,\\
&y_2-y_3=-(\mu_2/M)[(2a+b)/(a+b)]\eta,\\
&z_1+z_4=(\mu_1/m)z,\\
&z_1-z_4=2^{\frac{1}{2}}q-(2a+b),\\
&z_2+z_3=-(\mu_1/M)z,\\
&z_2-z_3=-2^{\frac{1}{2}}\zeta-b,
\end{aligned}\tag{2}$$

where

$$\mu_1=2mM/(m+M)$$

and

$$\mu_2=2mM(a+b)^2/[Mb^2+m)2a+b)^2].$$

The kinetic energy, $T=(\tfrac{1}{2})\sum m_i(\dot{x}_i^2+\dot{y}_i^2+\dot{z}_i^2)$, is the following function of the intermediate coordinates:

$$T_V=(\tfrac{1}{2})[\mu_1(\dot{x}^2+\dot{y}^2+\dot{z}^2)+\mu_2(\dot{\xi}^2+\dot{\eta}^2)+m\dot{q}^2+M\dot{\zeta}^2].\tag{3}$$

In these same coordinates the harmonic part of the potential energy takes the form

$$U_0=(\tfrac{1}{2})[k_1\zeta^2+2k_{12}\zeta q+k_2q^2+k_3z^2+k_4(x^2+y^2)+k_5(\xi^2+\eta^2)].\tag{4}$$

By using (3) and (4) in Lagrange's determinantal equation, $|\lambda T_V-U_0|=0$, one can obtain the normal frequencies ω_i (measured in cm^{-1}) which

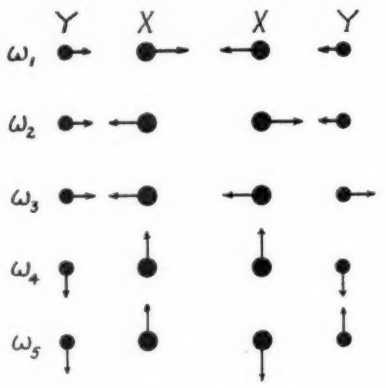

FIG. 2. Normal modes.

are related to the roots λ_i of the determinant by $\omega_i=(\lambda_i^{\frac{1}{2}}/2\pi c)$ (where c=velocity of light in cm/sec.). The roots λ_i are given explicitly by the following equations:

$$\left.\begin{matrix}\lambda_1\\ \lambda_2\end{matrix}\right\}=2^{-1}\{[(k_1/M)+(k_2/m)]\mp[((k_2/m)-(k_1/M))^2+4k_{12}^2/mM]^{\frac{1}{2}}\},\tag{5}$$

$$\lambda_3=(k_3/\mu_1);\quad \lambda_4=(k_4/\mu_1);\quad \lambda_5=(k_5/\mu_2).$$

The normal modes associated with these frequencies are illustrated in Fig. 2. The normal coordinates corresponding to the nondegenerate modes ω_1, ω_2, and ω_3 are

$$\begin{aligned}
&Q_1=\alpha m^{\frac{1}{2}}q+\beta M^{\frac{1}{2}}\zeta,\\
&Q_2=\beta m^{\frac{1}{2}}q-\alpha M^{\frac{1}{2}}\zeta,\\
&Q_3=\mu_1^{\frac{1}{2}}z,
\end{aligned}\tag{6}$$

where α and β are defined as follows:

$$\left.\begin{matrix}\alpha\\ \beta\end{matrix}\right\}=\pm(\tfrac{1}{2})^{\frac{1}{2}}\{1\mp[((k_2/m)-(k_1/M))^2/(4k_{12}^2/mM+[(k_2/m)-(k_1/M)]^2)]^{\frac{1}{2}}\}^{\frac{1}{2}}.\tag{7}$$

Corresponding to the two twofold degenerate modes ω_4 and ω_5 are the normal coordinates

$$R_4=\mu_2^{\frac{1}{2}}\xi,\quad S_4=\mu_2^{\frac{1}{2}}\eta,\quad R_5=\mu_1^{\frac{1}{2}}x,\quad S_5=\mu_1^{\frac{1}{2}}y.\tag{8}$$

In terms of the normal coordinates T_V and U_0 are

$$\begin{aligned}
T_V&=(\tfrac{1}{2})[\dot{Q}_1^2+\dot{Q}_2^2+\dot{Q}_3^2+\dot{R}_4^2+\dot{S}_4^2+\dot{R}_5^2+\dot{S}_5^2],\\
U_0&=(\tfrac{1}{2})[\lambda_1Q_1^2+\lambda_2Q_2^2+\lambda_3Q_3^2+\lambda_4(R_4^2+S_4^2)+\lambda_5(R_5^2+S_5^2)].
\end{aligned}\tag{9}$$

It is convenient in the subsequent discussion to introduce dimensionless coordinates,

$q_1=(\lambda_1^{\frac{1}{2}}/\hbar^{\frac{1}{2}})Q_1$, etc., with conjugate momenta, $p_{q_1}=(\partial T/\partial\dot{q}_1)$, in terms of which the zero-order vibrational energy can be written in the Hamiltonian form

$$H_{0V}=(hc/2)\left\{\sum_{i=1}^{3}\omega_i(p_{q_i}^2/\hbar^2+q_i^2)+\sum_{k=4}^{5}\omega_k((p_{r_k}^2+p_{s_k}^2)/\hbar^2+(r_k^2+s_k^2))\right\}. \quad (10)$$

The anharmonic part of the potential energy contains the following cubic and quartic terms consistent with the symmetry of the normal modes:

$$U_1=hc\left\{\sum_{i=1}^{2}[\beta_{iii}q_i^3+\beta_{i33}q_iq_3^2+\sum_{k=4}^{5}\beta_{ikk}q_i(r_k^2+s_k^2)]+\beta_{122}q_1q_2^2+\beta_{211}q_2q_1^2\right\}, \quad (11)$$

$$U_2=hc\left\{\sum_{i=1}^{3}[\gamma_{iiii}q_i^4+\sum_{i\neq l=1}^{3}\gamma_{iill}q_i^2q_l^2]+\sum_{k=4}^{5}(r_k^2+s_k^2)[\gamma_{kkkk}(r_k^2+s_k^2)+\gamma_{12kk}q_1q_2+\sum_{i=1}^{3}\gamma_{iikk}q_i^2]+\sum_{i=1}^{2}\sum_{i\neq l=1}^{2}\gamma_{iill}q_i^3q_l+\gamma_{1233}q_1q_2q_3^2+\gamma_{4455}(r_4^2+s_4^2)(r_5^2+s_5^2)\right\}, \quad (12)$$

in which the constants β_{iii}, γ_{iiii}, etc., have the dimensions cm^{-1}.

In the following quantum-mechanical treatment of the problem it will be found suitable to replace the coordinates associated with the twofold degenerate modes by polar coordinates according to the transformations

$$r_4=\rho_4\cos\phi_4;\quad r_5=\rho_5\cos\phi_5,\qquad s_4=\rho_4\sin\phi_4;\quad s_5=\rho_5\sin\phi_5. \quad (13)$$

3. The Quantum-Mechanical Hamiltonian

The appropriate quantum-mechanical Hamiltonian was derived by the method of Wilson and Howard[8] with the modification suggested by Sayvetz[5] for the case of a linear polyatomic molecule. The Hamiltonian was set up to include terms of zero-, first-, and second-order of approximation as $H=H_0+\lambda H_1+\lambda^2H_2$. The Hamiltonian thus obtained was transformed by a contact transformation to give $H'=THT^{-1}$ according to the method suggested by Shaffer, Nielsen and Thomas.[9] In this procedure the transformation operator T has the form $T=e^{i\lambda S}$ and the transformed Hamiltonian is given by

$$H'=H_0'+\lambda H_1'+\lambda^2H_2',$$

where

$$H_0'\equiv H_0,\quad H_1'=H_1+i(SH_0-H_0S),\quad H_2'=H_2+(i/2)[S(H_1+H_1')-(H_1+H_1')S]. \quad (14)$$

The appropriate form of the function S has been discussed by Silver and Shaffer.[10] For the Y_2X_2 problem S may be chosen so that $H_1'=0$, and the calculation of the higher order contributions to the energy is thereby simplified.

The zero-order terms in H' are given by

$$H_0'=H_0=H_{0V}+[1/(2I_e)](P_x^2+P_y^2), \quad (15)$$

where H_{0V} is given by Eq. (10). $I_e=(mM/\mu_2)(a+b)^2$ is the equilibrium value of the moment of inertia about the x or y axis of the model, and P_x and P_y are the components of total angular momentum about the x and y axes.

[9] W. H. Shaffer, H. H. Nielsen and L. H. Thomas, Phys. Rev. **56**, 895 (1939).
[10] S. Silver and W. H. Shaffer, J. Chem. Phys. **9**, 599 (1941).

The second-order portion of H' contains the following terms:

$$
\begin{aligned}
H_2' = &-(1/(2I_e^3))[(\delta^2/\lambda_1)+(\gamma^2/\lambda_2)](P_x^2+P_y^2)^2+(1/(2I_e))\{a_{11}q_1^2+a_{22}q_2^2+a_{33}q_3^2+a_{44}\rho_4^2+a_{55}\rho_5^2\}(P_x^2+P_y^2)\\
&+(1/I_e)\{b_{44}(r_4^2P_x^2+s_4^2P_y^2)+b_{55}(r_5^2P_x^2+s_5^2P_y^2)\}+\hbar^2/(2I_e)\\
&-(i\hbar/I_e)[\delta^2 q_1 p_{q_1}+\gamma^2 q_2 p_{q_2}-\gamma\delta(q_2 p_{q_1}+q_1 p_{q_2})]\\
&-hc\Big\{\sum_{i=1}^{2}(\beta_{iii}^2/\omega_i)[(3/\hbar^2)p_{q_i}^2 q_i^2+1+(3/2)q_i^4]\\
&+\sum_{i=1}^{2}\sum_{i\neq l=1}^{3}(\beta_{ill}^2/[2\omega_i(4\omega_l^2-\omega_i^2)])[(2\omega_l^2-\omega_i^2)q_l^4+4\omega_i\omega_l q_i^2 q_l^2+2\omega_l^2 q_i^2 p_{q_l}^2/\hbar^2]\\
&+\sum_{i=1}^{2}\sum_{k=4}^{5}(\beta_{ikk}^2/[2\omega_i(4\omega_k^2-\omega_i^2)])[(2\omega_k^2-\omega_i^2)\rho_k^4+4\omega_k\omega_i\rho_k^2 q_i^2+4\omega_k^2(v_k+1)\rho_k^2-2\omega_k^2\rho_k^4]\\
&+3\sum_{i=1}^{2}\sum_{i\neq l=1}^{3}(\beta_{iii}\beta_{ill}/\omega_i)q_i^2 q_l^2+3\sum_{i=1}^{2}\sum_{k=4}^{5}(\beta_{iii}\beta_{ikk}/\omega_i)q_i^2\rho_k^2+(\beta_{122}\beta_{133}/\omega_1)q_1^2 q_3^2\\
&+(\beta_{211}\beta_{233}/\omega_2)q_1^2 q_3^2+\sum_{i=1}^{2}\sum_{i\neq l=1}^{3}\sum_{k=4}^{5}(\beta_{ill}\beta_{ikk}/\omega_i)q_l^2\rho_k^2\\
&+\sum_{i=1}^{2}(\beta_{i44}\beta_{i55}/\omega_i)\rho_4^2\rho_5^2\Big\}+(1/(2I_e))(p_x^2+p_y^2)+U_2,
\end{aligned}
$$

where

$$
\begin{aligned}
\gamma &= [(\mu_2/2m)^{\frac{1}{2}}(b/(a+b))\alpha+(\mu_2/2M)^{\frac{1}{2}}((2a+b)/(a+b))\beta],\\
\delta &= [(\mu_2/2m)^{\frac{1}{2}}(b/(a+b))\beta-(\mu_2/2M)^{\frac{1}{2}}((2a+b)/(a+b))\alpha],
\end{aligned}
\tag{17}
$$

and $\gamma^2+\delta^2=1$. p_x and p_y, the components of internal angular momentum about the x and y axes, respectively, have the following form:

$$
\begin{aligned}
p_x = &\{\gamma[(\omega_1/\omega_5)^{\frac{1}{2}}s_5 p_{q_1}-(\omega_5/\omega_1)^{\frac{1}{2}}q_1 p_{s_5}]+\delta[(\omega_2/\omega_5)^{\frac{1}{2}}s_5 p_{q_2}-(\omega_5/\omega_2)^{\frac{1}{2}}q_2 p_{s_5}]\\
&+[(\omega_3/\omega_4)^{\frac{1}{2}}s_4 p_{q_3}-(\omega_4/\omega_3)^{\frac{1}{2}}q_3 p_{s_4}]\},\\
p_y = -&\{\gamma[(\omega_1/\omega_5)^{\frac{1}{2}}r_5 p_{q_1}-(\omega_5/\omega_1)^{\frac{1}{2}}q_1 p_{r_5}]+\delta[(\omega_2/\omega_5)^{\frac{1}{2}}r_5 p_{q_2}-(\omega_5/\omega_2)^{\frac{1}{2}}q_2 p_{r_5}]\\
&+[(\omega_3/\omega_4)^{\frac{1}{2}}r_4 p_{q_3}-(\omega_4/\omega_3)^{\frac{1}{2}}q_3 p_{r_4}]\}.
\end{aligned}
\tag{18}
$$

The quantities a_{11}, a_{22}, b_{44}, etc., which occur in H_2', are defined as follows:

$$
\begin{aligned}
a_{11} &= (\hbar/I_e)\lambda_1^{-1}\{3-4\gamma^2[\lambda_5/(\lambda_5-\lambda_1)]\}+4\pi c(\hbar/I_e)^{\frac{1}{2}}[3\delta\lambda_1^{-\frac{3}{4}}\beta_{111}-\gamma\lambda_2^{-\frac{3}{4}}\beta_{211}],\\
a_{22} &= (\hbar/I_e)\lambda_2^{-1}\{3-4\delta^2[\lambda_5/(\lambda_5-\lambda_2)]\}+4\pi c(\hbar/I_e)^{\frac{1}{2}}[-3\gamma\lambda_2^{-\frac{3}{4}}\beta_{222}+\delta\lambda_1^{-\frac{3}{4}}\beta_{122}],\\
a_{33} &= (\hbar/I_e)\lambda_3^{-1}[(3\lambda_3+\lambda_4)/(\lambda_3-\lambda_4)]+4\pi c(\hbar/I_e)^{\frac{1}{2}}[\delta\lambda_1^{-\frac{3}{4}}\beta_{133}-\gamma\lambda_2^{-\frac{3}{4}}\beta_{233}],\\
a_{44} &= 4\pi c(\hbar/I_e)^{\frac{1}{2}}[\delta\lambda_1^{-\frac{3}{4}}\beta_{144}-\gamma\lambda_2^{-\frac{3}{4}}\beta_{244}],\\
a_{55} &= 4\pi c(\hbar/I_e)^{\frac{1}{2}}[\delta\lambda_1^{-\frac{3}{4}}\beta_{155}-\gamma\lambda_2^{-\frac{3}{4}}\beta_{255}],\\
b_{44} &= (\hbar/(2I_e))\lambda_4^{-1}[(3\lambda_4+\lambda_3)/(\lambda_4-\lambda_3)],\\
b_{55} &= (\hbar/(2I_e))\lambda_5^{-1}\{\gamma^2[(3\lambda_5+\lambda_1)/(\lambda_5-\lambda_1)]+\delta^2[(3\lambda_5+\lambda_2)/(\lambda_5-\lambda_2)]\}.
\end{aligned}
\tag{19}
$$

4. The Eigenvalues

The eigenvalues of H_0' and H_2' have been found by a method similar to that employed by Silver and Shaffer[10] for the XY_3 model. After collection of terms the total energy, through second order of approximation, has the form

$$
E = E_0'+E_2' = hc(G_V+F_R). \tag{20}
$$

rational term value G_V is given by

$$+\sum_{n=1}^{5}\omega_n(v_n+g_n/2)+\sum_{n=1}^{5}x_{nn}(v_n+g_n/2)^2 + \sum_{n=1}^{5}\sum_{n>n'=1}^{4}x_{nn'}(v_n+g_n/2)(v_{n'}+g_{n'}/2)+\sum_{k=4}^{5}X_{kk}(l_k^2-1), \quad (21)$$

v_n is the vibrational quantum number associated with the normal frequency ω_n, and g_n is gree of degeneracy of the same mode; $g_1=g_2=g_3=1$; $g_4=g_5=2$; and l_k is the quantum number ted with the internal angular momentum $p_{\phi k}$ arising from the twofold degenerate mode ω_k. assume the values $\pm v_k$, $\pm(v_k-2)$, $\cdots$, ±1 or 0. The parameters occurring in (21) are defined ws:

$$G_0=-(7/16)\sum_{i=1}^{2}(\beta_{iii}^2/\omega_i)+(3/16)\sum_{i=1}^{2}\sum_{i\neq l=1}^{3}(\beta_{ill}^2\omega_i)/(4\omega_l^2-\omega_i^2)+(3/8)\sum_{i=1}^{3}\gamma_{iiii},$$

$$x_{11}=(1/4)\{6\gamma_{1111}-15(\beta_{111}^2/\omega_1)-[(8\omega_1^2-3\omega_2^2)\beta_{211}^2/\omega_2(4\omega_1^2-\omega_2^2)]\},$$

$$x_{22}=(1/4)\{6\gamma_{2222}-15(\beta_{222}^2/\omega_2)-[(8\omega_2^2-3\omega_1^2)\beta_{122}^2/\omega_1(4\omega_2^2-\omega_1^2)]\},$$

$$x_{33}=(1/4)\{6\gamma_{3333}-\sum_{i=1}^{2}[(8\omega_3^2-3\omega_i^2)\beta_{i33}^2/\omega_i(4\omega_3^2-\omega_i^2)]\},$$

$$x_{kk}=(1/4)\{6\gamma_{kkkk}-\sum_{i=1}^{2}[(8\omega_i^2-3\omega_k^2)\beta_{ikk}^2/\omega_k(4\omega_i^2-\omega_k^2)]\}, \quad k=4,5,$$

$$x_{12}=\{\gamma_{1122}-3(\beta_{111}\beta_{122}/\omega_1)-3(\beta_{222}\beta_{211}/\omega_2)-2\beta_{122}^2[\omega_2/(4\omega_2^2-\omega_1^2)]-2\beta_{211}^2[\omega_1/(4\omega_1^2-\omega_2^2)]\},$$

$$x_{13}=\{\gamma_{1133}-(\beta_{211}\beta_{233}/\omega_2)-3(\beta_{111}\beta_{133}/\omega_1)-2\beta_{133}^2[\omega_3/(4\omega_3^2-\omega_1^2)]\},$$

$$x_{14}=\{\gamma_{1144}-(\beta_{211}\beta_{244}/\omega_2)-3(\beta_{111}\beta_{144}/\omega_1)-2\beta_{144}^2[\omega_4/(4\omega_4^2-\omega_1^2)]\}, \quad (22)$$

$$x_{15}=\{\gamma_{1155}-(\beta_{211}\beta_{255}/\omega_2)-3(\beta_{111}\beta_{155}/\omega_1)-2\beta_{155}^2[\omega_5/(4\omega_5^2-\omega_1^2)+\gamma^2B_e[(\omega_1/\omega_5)+(\omega_5/\omega_1)]\},$$

$$x_{23}=\{\gamma_{2233}-(\beta_{122}\beta_{133}/\omega_1)-3(\beta_{222}\beta_{233}/\omega_2)-2\beta_{233}^2[\omega_3/(4\omega_3^2-\omega_2^2)]\},$$

$$x_{24}=\{\gamma_{2244}-(\beta_{122}\beta_{144}/\omega_1)-3(\beta_{222}\beta_{244}/\omega_2)-2\beta_{244}^2[\omega_4/(4\omega_4^2-\omega_2^2)]\},$$

$$x_{25}=\{\gamma_{2255}-(\beta_{122}\beta_{155}/\omega_1)-3(\beta_{222}\beta_{255}/\omega_2)-2\beta_{255}^2[\omega_5/(4\omega_5^2-\omega_2^2)]+\delta^2B_e[(\omega_2/\omega_5)+(\omega_5/\omega_2)]\},$$

$$x_{34}=\{\gamma_{3344}-(\beta_{133}\beta_{144}/\omega_1)-(\beta_{233}\beta_{244}/\omega_2)+B_e[(\omega_3/\omega_4)+(\omega_4/\omega_3)]\},$$

$$x_{35}=\{\gamma_{3355}-(\beta_{133}\beta_{155}/\omega_1)-(\beta_{233}\beta_{255}/\omega_2)\},$$

$$x_{45}=\{\gamma_{4455}-(\beta_{144}\beta_{155}/\omega_1)-(\beta_{244}\beta_{255}/\omega_2)\},$$

$$X_{kk}=-(1/4)\{2\gamma_{kkkk}+\sum_{i=1}^{2}\beta_{ikk}^2[\omega_i/(4\omega_k^2-\omega_i^2)]\}, \quad k=4,5$$

in which $B_e=(h/(8\pi^2cI_e))$.

The rotational term F_R can be written as

$$F_R=B_v[J(J+1)-(l_4+l_5)^2]-D[J(J+1)-(l_4+l_5)^2]^2, \quad (23)$$

where J is the quantum number associated with the total angular momentum ($P^2=J(J+1)\hbar^2$) and may assume values such that $J\geqslant|l_4+l_5|$. The constants B_v and D are defined as follows:

$$B_v=B_e-\sum_{n=1}^{5}\alpha_n(v_n+g_n/2), \quad (24)$$

$$D=4B_e^3[(\gamma^2/\lambda_2)+(\delta^2/\lambda_1)],$$

in which

$$\alpha_i = -a_{ii}B_e, \quad i=1, 2, 3,$$
$$\alpha_k = -(a_{kk}+b_{kk})B_e, \quad k=4, 5.$$

The selection rules governing transitions between eigenstates have been given by Dennison.[2]

5. Conclusions

From a comparison of the energy expressions of Wu and Kiang[4] and Wu[6] with those obtained in this paper it is seen that the purely vibrational terms check exactly. However, there are several points of disagreement in the rotational terms: Wu[6] completely omitted the terms quartic in J, l_4 and l_5, which arise from the centrifugal stretching of the molecule. There are several errors in Wu's expressions for the parameters α_n occurring in the expression (24) for the effective rotational constant B_v. His expressions for α_4 and α_5 contain certain terms depending only on the masses and internuclear distances which should not be present and which occur in his expressions because of an error in setting down the quantity A' of his paper. We also obtain different expressions for the numerators of the quantities involving resonance denominators in the α_n.

The corrections pointed out here may have considerable effect on the interpretation of the fine structure of the near infra-red bands of linear Y_2X_2 molecules and will cause some changes in Wu's values of the anharmonic constants of acetylene.

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The Region of Critical Solution of Binary Liquids, Evidence for an Anomalous First-Order Transition in the System Triethyl Amine-Water*

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The change of fugacity with composition has been investigated in the liquid system triethyl amine-water in the temperature region adjacent to the temperature of critical solution. It has been shown that within experimental error this change is zero for a range of at least 5°C on the one phase side, and for compositions of liquid between 20 and 50 weight percent. This is taken to be evidence for the existence of a range of anomalous first-order transition adjacent to the critical temperature. Values of change of fugacity with composition have been determined sufficiently precisely to be in definite disagreement with simple conclusions drawn from the concept of the continuity of states.

Introduction

STUDIES by Maass and others[1,2] have shown that several densities of a gas may co-exist without an interface within a small temperature-pressure range just above the critical temperature and pressure. Due to gravity, a portion of higher density settles to the bottom of the gas container. Also due to gravity there is a slight increase of pressure with depth (about 0.01 mm pressure per mm depth). Maass investigated the rate of change of density with depth, and found a region in which the density change was apparently discontinuous within at least a few mm change in depth. This corresponds to a pressure-

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[1] Maass and Geddes, Phil. Trans. Roy. Soc. London **A236**, 303–32 (1937).

[2] Maass and McIntosh, Can. J. Research **B16**, 289–301 (1938).

volume curve for which a finite portion may be drawn as a straight line of zero slope, pressure independent of volume for a finite density range. The algebraic function corresponding to this complete curve is non-analytic; and in this respect it departs from the van der Waals and similar formulations which lead to analytic functions of necessarily finite slope for this portion of the P-V diagram.

Usually, the pressure-volume isotherms of the critical region of a gas are classified in two sets. One set consists of those isotherms with a slope discontinuity (first-order transition) at temperatures below the critical; and the other set consists of those isotherms above the critical temperature which are, of course, continuous, and of which only the one at the critical temperature is assumed to have an inflection point of zero slope. Maass' observations may be regarded as evidence for a third set of isotherms inserted between the two above sets of the van der Waals type curves. Of this third set each isotherm has no discontinuity in slope, but has a horizontal range of finite volume interval. This range of finite extent in temperature and density is the region of the anomalous first-order transition.

It is interesting that the above third region was commonly accepted before the introduction of the van der Waals concept of the continuity of the states.

Theoretical work[3] has predicted behavior of

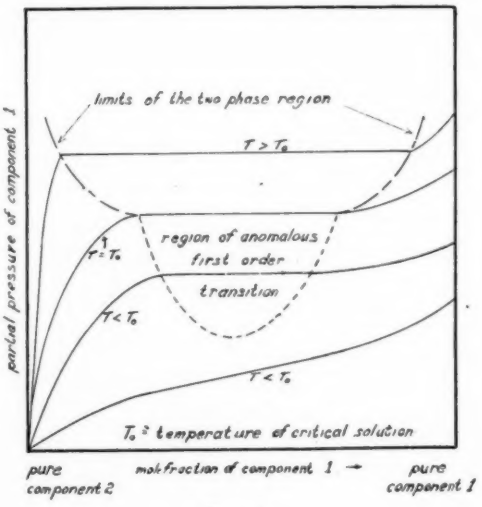
limits of the two phase region
T > T₀
region of anomalous first order transition
T = T₀
T < T₀
T < T₀
T₀ = temperature of critical solution
partial pressure of component 1
pure component 2
mol fraction of component 1 →
pure component 1

FIG. 1.

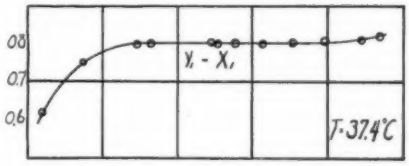

FIG. 2. CS_2—MeOH system. The curves marked Y_1-X_1 are in mole fraction units; those marked U_1-W_1 are in weight fraction units.

the above type for gas to liquid transitions. We feel, however, that this behavior may not be limited to gas-liquid transitions; but may be a property of all critical regions.[4]

The purpose of this research is to look for a set of isotherms showing an anomalous first-order transition for systems of two partially miscible liquid components. By analogy to one component systems, one might expect to find such a transition in a small temperature-pressure range adjacent to the temperature of critical miscibility producing but a single liquid phase. In the case of a binary liquid mixture, the criterion for such an anomalous first-order transition would be that for a finite temperature and composition range one would have the chemical potential, or fugacity, of each component independent of liquid composition, although only one (liquid) phase would be apparently present.

Figure 1 shows a plot of the partial pressure (essentially equal to fugacity) of one component against the mole fraction of this component in the liquid, in the region of a typical lower critical point. Isotherms are drawn for various temperatures. The lower dotted curve encloses the hypothetical region of first-order anomalous transition, in which we wish to show the fugacity to be independent of composition.

Actually, in this work the mole fraction, y_1, of one component in the vapor, in equilibrium with the liquid of mole fraction, x_1, of this component, was measured. A determination of the pressure is unnecessary since it follows that if y_1 is independent of x_1 the fugacity of both components is independent of the liquid composition.

To be more explicit, for an isotherm to contain an anomalous first-order transition, two conditions must be fulfilled. They are: first, dy_1/dx_1 must be everywhere continuous; second,

[3] J. E. Mayer and S. F. Harrison, J. Chem. Phys. **6**, 87 (1938).

[4] Joseph E. Mayer and S. F. Streeter, J. Chem. Phys. **7**, 1019 (1939).

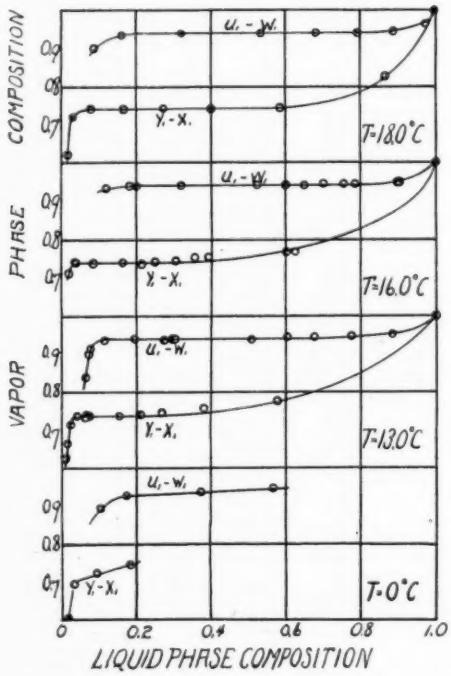

FIG. 3. Et_3N-H_2O system. The curves marked Y_1-X_1 are in mole fraction units; those marked U_1-W_1 are in weight fraction units.

$dy_1/dx_1=0$ for a finite range of values of x_1. The first requirement is presumably fulfilled since we deal with but a single liquid phase. The second requirement, however, must be demonstrated.

Liquid pairs were selected for this work which possessed critical regions at one atmosphere pressure and at readily available temperatures. The two systems studied were carbon disulfide-methyl alcohol and triethyl amine-water. The carbon disulfide-methyl alcohol system is two phase below about 37°C, and the liquids are miscible in all proportions above this. The triethyl amine-water system has a two-phase region *above* 18.4°C, and is one phase in all proportions below this critical temperature. As first considerations indicated that the carbon disulfide-methyl alcohol system would be suitable, it was used for the preliminary work.

It was first necessary to know the carbon disulfide-methyl alcohol critical temperature. Published values are poor, ranging from 35° to 40°C,[5,6] possibly due to the fact that the critical temperature of this system is quite sensitive to small amounts of impurity, and that the critical temperature seems to rise about one degree centigrade during the first 24–48 hours after the solution is prepared. Because of this lack of agreement, the critical temperature (about 37°C) for the particular carbon disulfide and methyl alcohol used was determined, and this value was taken as a probable lower boundary of the set of anomalous isotherms. Since the temperature range of the anomalous region is expected to be at least several degrees wide, 37.4°C was picked as a temperature likely to result in an isotherm showing an anomalous first-order transition. The first experimental work was done at this temperature.

The necessary points for the curve were obtained by slowly evaporating, in an evacuated system, about two percent of a solution of carbon disulfide and methyl alcohol of mole fraction of carbon disulfide, x_1, and measuring the relative volumes of the two phases into which the condensate separated at zero degrees centigrade. The phase volume readings were then converted into mole fraction units, y_1, of carbon disulfide in the vapor. Thus by distilling a number of solutions with values of x_1 ranging from 0 to 1 a complete set of values of y_1 and x_1 (and hence a complete isotherm) was obtained. The difficulties arising from the use of the carbon disulfide-methyl alcohol solutions made the work slow and the reproducibility of the results poor. However, a very definite indication of an anomalous first-

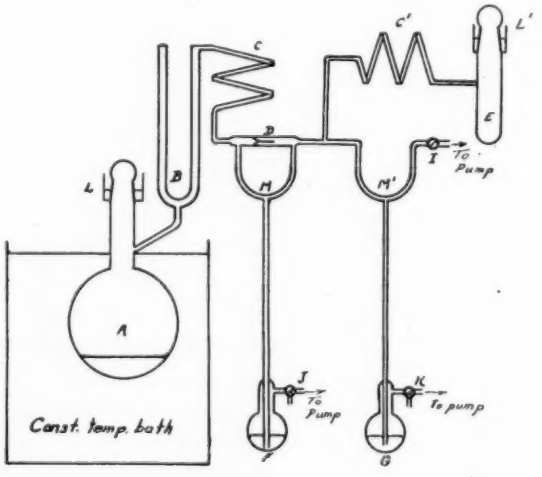

FIG. 4.

[5] V. Rothmund, Zeits. f. physik. Chemie **26**, 433 (1898).
[6] E. C. McKelvy and D. H. Simpson, J. Am. Chem. Soc. **44**, 105 (1922).

order transition was obtained; and the section of the isotherm of negligible slope was unexpectedly wide (Fig. 2).

On the basis of experience with the carbon disulfide-methyl alcohol system, it was decided that better results could be obtained with the triethyl amine-water system. Experience has proven that the advantages are numerous. The solutions can be analyzed by acid-base titration.[7] The vapor pressure of the system is low (about 5 cm) near the critical temperature (18.4° ±0.2°C). The critical temperature is quite reproducible as is shown by the uniformity of published results.[5,8] The vapor does not dissolve rapidly in stopcock grease which permits the use of stopcocks protected by mercury seals. Since the temperature of distillation is below room temperature, no precautions need be taken to prevent the condensation of triethyl amine-water vapor in parts of the apparatus commonly left at room temperature.

The experimental procedure was fundamentally the same as that used with the carbon disulfide-methyl alcohol system; the equilibrium mole fraction, y_1, of triethyl amine in the vapor corresponding to a series of triethyl amine-water solutions of triethyl amine mole fraction, $0 \leq x_1 \leq 1$, was determined. From this series of values, the graph of the isotherm may be drawn.

Figure 3 shows the four isotherms obtained. They are presented as plots of the vapor and liquid mole fractions, $y_1 = y_1(x_1)$. It is seen that each curve has a wide flat section, and if we assume that in this region, $y_1(x_1) = W'x_1 + W$, the slope W' for three of the isotherms calculated by least squares is found to be zero within the experimental error.

Experimental Method, Et_3N-H_2O

The determination of each pair of values y_1 and x_1 was carried out in two steps. Firstly, the partial pressure of air in the system was decreased to a small value; and secondly, the equilibrium evaporation of a sample of vapor was carried out. Air had to be removed from the apparatus so that the flow of vapor from the evaporator to the condenser would be mass flow, not diffusion.

The water used was purified by a single distillation in a tin still. The triethyl amine used was an Eastman Kodak Company product fractionated to a boiling range of 89.3°–89.4°C (corrected) (Landolt Börnstein value, 89.4°C), $n_0^{25} = 1.3997$, and percent Et_3N as base = 100.27.

Distillations were carried out from a water bath thermostat held constant to within ±0.01°C.

Figure 4 is a drawing of the apparatus used for the triethyl amine-water system; its use is described below.

Approximately 100 cc of a solution of desired mole fraction, x_1, of triethyl amine was poured into the 500 cc flask A; and the mercury seal stoppers inserted at L and L'. All of the stopcocks were adjusted to permit gas to flow out of the apparatus to the pump; dry ice and methyl alcohol were placed in trap B; and the apparatus was pumped out. The trap B, which did not interfere with the removal of air, condensed vapor coming from A and returned the condensate. Thus very little of the solution in A was lost by evaporation during pumping. When pumping was complete, stopcock I was closed, and J was adjusted so that mercury would rise from flask F to close the U-tube M. The cooling mixture was removed from trap B, and the flask A was mechanically shaken until its contents were at bath temperature. The partial pressure of air in the apparatus was reduced to a value probably considerably less than 1 mm by this procedure; but the vapor filling the apparatus was not of the equilibrium composition with respect to the liquid at the bath temperature in A. To remedy this, stopcock I was opened; and, with U-tube M closed, the system was again pumped. Because the vapor had to flow through the fine capillary D, the evaporation in A was slow, (about 1 to 4 cc of liquid per hour); and, because the flask A was shaken, its contents were maintained at bath temperature. These conditions insured that the vapor filling the apparatus at the end of this second pumping was of the equilibrium composition. Pumping being completed, stopcock I was closed and K was adjusted to permit mercury to rise from flask G and close the U-tube M'. The next step was to cool the condenser E in a dry ice-methyl alcohol bath, causing vapor to flow through the fine capillary D by the path B, C, D, and C' to E where it of course condensed. The vapor pressure over the liquid was read by means of a mercury manometer (not shown in the figure) attached to A. After about a half hour approximately one cc of condensate collected and the distillation was stopped by filling the apparatus with dry air. Approximately 0.3 g samples

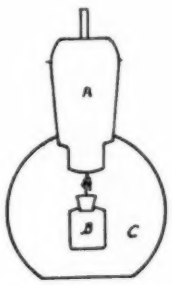

FIG. 5.

[7] H. Meyer, *Analyse Organischer Verbindungen* (J. Springer, Berlin 1922), p. 945.
[8] F. Guthrie, Phil. Mag. [5] **18**, 504 (1884).

TABLE I. *Triethylamine-water isotherms; w_1 = weight fraction Et_3N in vapor, u_1 weight fraction in liquid.*

	EQUATIONS	RANGE
18° Isotherm	$0.9426-0.00143u_1=w_1$	$0.25\leq u_1 0\leq .80$
16°	$0.9401+0.00096u_1=w_1$	$0.18\leq u_1 0\leq .60$
13°	$0.9391+0.00011u_1=w_1$	$0.20\leq u_1 0\leq .50$
0°	$0.9204+0.04092u_1=w_1$	$0.17\leq u_1 0\leq .56$

Precision of Results

ISOTHERM TEMP.	INTERCEPT a	SLOPE b	DEVIATION OF EXP. PTS. FROM LINE R.M.S. DEV.	AV. DEV.	PROB. ERROR OF SLOPE b
18°	0.9426	−0.00143	0.037	0.042	0.0017
16°	0.9401	0.00096	0.095	0.064	0.0022
13°	0.9391	0.00011	0.067	0.051	0.0029
0°	0.9204	0.04092	0.041	0.040	0.0027

Arithmetic mean of b for 18°, 16°, and 13° isotherms equals −0.00012.

of the solutions in A and in E were each transferred to a weighing bottle, weighed, dissolved in excess standard (0.1N) HCl (25 cc), and each solution was back titrated with (0.1N) standard base. A 10 cc microburette was used in these back titrations.

From the titration data, the mole percents, y_1 and x_1, for the solutions in E and A, respectively, were calculated.

Difficulty was at first experienced in transferring a triethyl amine-water sample from the apparatus to a weighing bottle, since triethyl amine was lost. This difficulty was overcome by the use of the apparatus shown in Fig. 5. Standard acid of the required volume was pipetted into flask C. The triethyl amine sample was pipetted into weighing bottle B and the glass stopper of B was firmly inserted. Weighing bottle B was weighed, and then suspended by a platinum hook from glass stopper A and the whole inserted in flask C as illustrated. Upon shaking, the weighing bottle B separated from its stopper and fell into the acid. Since this weighing bottle B was opened in a closed flask, none of the weighed sample of triethyl amine-water could escape solution in the acid.

A mixture—0.02 percent methyl orange and 0.02 percent brom cresol purple—was used as the indicator in these titrations. The methyl orange indicated the approach of the end point, and the brom cresol purple was used to define the end point.

The end point range was about 0.01 cc.

Four isotherms at the temperatures 18°, 16°, 13°, and 0° were obtained. In order to select the temperature for the isotherm nearest the upper boundary of the single phase region, it was necessary to determine the consolute curve for the triethyl amine-water system. This was done by the method of Rothmund.[5] This consists of determining the temperatures at which turbidity appears or disappears through the range of triethyl amine-water mole fraction, $0\leq x_1\leq 1$.

Errors

The reproducibility of the total pressure readings (which are not essential to our argument) indicates that they are probably good to ±0.2 mm, the slight variations occasionally observed being regarded as due to residual air. Measurements similar to these in which the observed pressures were in general higher were made by R. T. Lattey.[9] It is felt that Lattey's higher readings were probably due to a less complete removal of air and hence that the total pressure readings given in Table III are the more reliable.

The expected average deviation of the component steps in the titrations of the triethyl amine-water samples are as follows: transfer of acid with a 25 cc pipette, 1/5000; end-point range for 20 cc titre, 1/2000; weighing of 0.3 g sample, 1/3000; and these values are in agreement with the observed average deviations which are about 1/2000. The precision of standardization of about 1/1000 of the acid and the base affects only the absolute, not the relative values of the weight percents of triethyl amine.

The absolute values of the weight fraction of triethyl amine in the vapor, u_1, may be in error as much as 0.5 percent due to uncertainty as to the amount of impurity. This figure is based on the fact that preliminary practice runs on unfractionated triethyl amine gave values differing from those given in Table III by as much as 1 percent.

It is to be emphasized that with the method used no superheating, which might have brought the liquid into the two-phase region, can occur.

RESULTS AND DISCUSSION

The outstanding result of the experiments is the seemingly horizontal character of a portion

TABLE II. *Carbon disulfide-methyl alcohol system*

MOLE FRAC. CS_2 IN LIQUID	VOL. MeOH PHASE = z AT 0°C	MOLE FRAC. CS_2 IN VAPOR
0.0446	0.614 cc	0.602
0.151	0.337	0.750
0.296	0.271	0.792
0.303	0.267	0.792
0.491	0.260	0.798
0.508	0.260	0.798
0.558	0.257	0.798
0.628	0.250	0.798
0.705	0.251	0.798
0.705	0.252	0.798
0.792	0.248	0.808
0.888	0.240	0.808
0.939	0.237	0.814

Total volume, methyl alcohol phase and carbon disulfide phase is 1 cc. Volume of the carbon disulfide phase is $(1-z)$ cc. The phase volumes, z, were obtained experimentally. The values given in the "Mole fraction CS_2 in the vapor" column were calculated from the z values, from the data of McKelvy and Simpson, reference 6 in text, on the composition of the CS_2 and MeOH phases, and with the assumption that the density of a carbon disulfide-methyl alcohol mixture is a linear function of composition. They may be as much as two or three percent in error.

[9] R. T. Lattey, J. Chem. Soc. **91**, 1959 (1907).

TABLE III. *Triethyl amine-water system.*

TEMP. °C	PERCENT Et_3N IN LIQUID WT. %	MOLE. %	PERCENT Et_3N IN VAPOR WT. %	MOLE. %	TOTAL PRESSURE CM HG	PARTIAL† PRESSURE Et_3N CM HG
	97.51	87.4	96.22	81.93	5.75	4.71
	97.32	86.6	96.35	82.84	5.75	4.76
	88.9	58.7	94.36	74.85		
	79.1	40.3	94.13	74.07	5.65	4.18
	68.2	27.6	94.21	74.35	5.65	4.20
18.0°	53.5	17.0	94.12	74.04	5.65	4.18
	32.3	7.8	94.23	74.42	5.65	4.20
	16.5	3.4	93.62	72.33	5.50	3.98
	15.9	3.3	93.81	72.97	5.47	3.99
	9.0	1.7	90.10	61.85	5.30	3.28
	17.71*	3.7	93.80*	72.94	5.50	4.01
	19.77*	4.2	93.90*	73.28	5.50	4.03
	90.26	62.28	94.92	76.90	5.15	3.96
	89.43	60.12	94.92	76.90	5.07	3.90
	78.52	39.44	94.49	75.34	5.00	3.77
	75.56	35.52	94.50	75.38	5.10	3.84
	70.86	30.23	94.27	74.56	4.99	3.72
	70.02	29.38	94.31	74.70	5.05	3.77
	65.50	25.27	94.12	74.03		
16.0°	65.17	25.00	94.14	74.11	4.97	3.64
	62.84	23.15	93.94	73.41		
	60.68	21.65	94.06	73.83	4.97	3.63
	54.02	17.31	94.26	74.53	4.93	3.66
	52.74	16.58	94.06	73.83		
	34.21	8.48	94.04	73.76		
	20.18	4.31	93.96	73.49	4.85	3.61
	18.16	3.80	94.07	73.86	4.85	3.63
	11.87	2.34	93.30	71.27	4.72	3.36
	88.45	57.70	95.12	77.64	4.32	3.35
	77.38	37.87	94.61	75.77	4.2	3.2
	67.43	26.95	94.29	74.63		
	60.22	21.24	94.09	73.94		
	50.78	15.53	93.93	73.38	4.1	2.94
	49.51	14.87	93.91	73.32	4.05	2.94
13.0°	30.75	7.33	93.83	73.04	4.00	2.93
	29.49	6.93	94.04	73.76	4.00	2.96
	27.48	6.32	93.85	73.11	4.00	2.93
	19.41	4.11	93.93	73.38	3.93	2.94
	11.55	2.27	93.29	71.24	3.78	2.69
	7.77	1.48	91.71	66.34	3.22	2.14
	7.00	1.32	90.26	62.28	3.07	1.91
	6.38	1.20	83.86	48.08	2.98	1.43
	56.37	18.71	94.32	74.74	1.75	1.31
0°	37.21	9.55	93.62	72.33	1.61	1.16
	17.35	3.60	92.72	69.41	1.50	1.04
	10.28	2.00	89.45	60.17	1.22	0.73

* The starred points were obtained using a different sample of Et_3N from that used for all of the other points. Due to this, the experimental values for percent Et_3N in the vapor, (17.71, 93.38) and (19.77, 93.48), were lower than was consistent with previous experiments. Hence, a correction (=+0.42) was applied to them. This correction was obtained by determining a point in the flat (28.88, 93.75) with the new Et_3N and subtracting this percent Et_3N in the vapor (=93.75) from the average of the corresponding values in the flat of the previous work, (=94.17).

† In calculating the partial pressures from the total pressures in the horizontal region an average of the total pressures for the corresponding temperature was used, namely, 5.65 cm at 18°C, 4.91 cm at 16°C, 4.01 cm at 13°C.

TABLE IV. *Consolute curve for* Et_3N-H_2O *system.*

WT. % Et_3N SINGLE LIQUID PHASE	TEMPERATURE AT WHICH TURBIDITY APPEARS
92.0	22.2°C
73.0	20.0
44.8	18.7
25.1	18.4
15.7	18.9

of the 18°, 16°, and 13° triethyl amine-water isotherms. This is particularly striking when contrasted to the relatively large slope of the corresponding section of the 0° isotherm of this system.

If the approximately horizontal part of each of these curves is assumed to have the analytic form, $w_1(u_1)=w_1=bu_1+a$, u_1 and w_1, respectively, liquid and vapor weight fractions of triethyl amine, the best value of the slope b, the probable error of b, and the deviation of the experimental points from the best straight line may be found by a least squares calculation. These values are given in Table I. This table also gives the approximate length of the fitted section of each isotherm.

Tables II and III give the experimental points, Table II for the carbon disulfide-methyl alcohol system and Table III for the triethyl amine-water system. Figure 1 is the graph of Table II and Fig. 3 contains the graphs of Table III.

The weight fraction isotherms of Fig. 3 are the ones which were used to calculate the values given in Table I.

Table IV gives the boundary of the two-phase region, consolute curve, for the triethyl amine-water system used.

Because of numerous uncertainties involved in the experimental work with the carbon disulfide-methyl alcohol system, and because of the comparatively large experimental error, an explicit discussion of this system is not given. However, many of the more general ideas of the following discussion apply equally to the carbon disulfide-methyl alcohol system and the triethyl amine-water system.

The calculated "most probable" slope b, change of weight percent triethyl amine in the vapor per unit change of weight percent in the

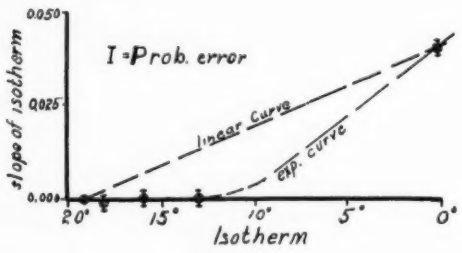

FIG. 6.

liquid phase, is the most interesting part of the results. These slopes, b, for the flat portions of the isotherms are nicely distributed around zero, there being one relatively large negative slope of -0.00143 and two smaller positive slopes of 0.00096 and 0.00011 for the 18°, 16° and 13°C isotherms, respectively (see Table I). Thermodynamically, a negative slope for the vapor composition-liquid composition isotherms of a two-component system is impossible. Hence, the slope, -0.00143, must be entirely due to experimental error, the correct value being either zero or positive. The arithmetic mean of the three slopes has a small negative value, -0.00012.

The experimental data have a rather small experimental error, and are completely in accord with the interpretation that the fugacity of the one component (and therefore also of the other) in the liquid is absolutely independent of composition between about 20 and 50 weight percent and between 18.4° and 13°C. It is, however, obvious that the data do not prove this conclusion to be exactly correct because of experimental error. Qualitative methods could not be used since no physical property of the system would change abruptly with decrease of the slope from a small value to zero. We seek some objective criterion by which we can say that the observed "slopes" are so low that they require a special explanation, and that therefore the explanation of assuming a true anomalous first-order transition, with zero slopes, is one of the simplest and most plausible.

Such a criterion was suggested to one of us by Professor Edward Teller. Somewhat modified it may be stated as follows. Suppose we know that any physical quantity, b, a function of one or more variables, $x_1, x_2 \cdots$ of any system, has a zero value at some value of the variables, $x_1^\circ, x_2^\circ, \cdots$. The mere fact that b is zero will not require that the change of b with any of the variables (or with some linear combination $z=ax_1+bx_2+\cdots$) also be zero, and if *both* $b=0$ and $db/dz=0$ at $z=z_0$ we require an explanation of *both* facts.

Specifically, the continuity of states concept assumes the existence of some naturally defined analytically continuous curves giving the isotherms $y_1=y_1(x_1)$ for temperatures on both sides of the critical point. On the one-phase side these curves are monotonically increasing. On the two-phase side the curves have a loop, and the experimental horizontal portion is obtained by bisecting the loop according to Maxwell's relation. If the slope‡ $b=dy_1/dx_1$ at the composition of the critical point is plotted against the temperature T, this slope would have positive values in the one phase region, be zero at the critical temperature T_c, and be negative in the two-phase region. If we develop as a power series in $T-T_c$ we can express b as

$$b=\alpha_1(T-T_c)+\alpha_2(T-T_c)^2+\cdots$$

and the linear coefficient α_1 would *not* be zero.

In Fig. 6 the slope b observed experimentally is plotted against the temperature T. The I's give the probable error. At the observed temperature (18.4°C) of the appearance of two phases this slope b is known to be zero. At 0°C it has the rather high value 0.04. The values at 18°, 16°, and 13° lie far beyond the experimental error off any linear or approximately linear curve connecting these two points.

We cannot claim to have proven that there exists a region for which the fugacity of one component is independent of composition. It appears, however, that we may definitely claim that the experimental observations are not only consistent with this interpretation but have sufficiently small error to lend strong credence to the supposition that a range of anomalous first-order transition occurs.

‡ Our slope b is actually in ratio of weight fractions.

The Entropy of Acetic Acid

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From third law measurements, vapor pressures and vapor densities, the entropy of the acetic acid monomer at 25° and one atmosphere is 69.4±1.0 e.u. The value 68.7 is calculated from the vapor phase ethyl acetate equilibrium. For a model based upon acetone and approximately representing free rotation the entropy would be 72.7. If there is only a single potential minimum in the hydroxyl group rotational cycle, the large deficiency below the free rotation value is explained without assuming an exceptionally high potential barrier. A brief discussion of the effect of the number of potential minima and their relative depth is appended, and a possible source of error in third law measurements is suggested.

THE entropy of the acetic acid monomer as a hypothetical perfect gas can be calculated from the third law entropy of the liquid and the heat of vaporization with the aid of the constants of the reaction

$$(CH_3COOH)_2 = 2CH_3COOH. \quad (1)$$

This procedure or its equivalent is made necessary by the wide deviations of acetic acid vapor from perfect gas behavior. The significance and accuracy of the result depend upon the completeness with which existing vapor density data may be used to describe the vapor as a mixture of two perfect gases in equilibrium according to Eq. (1). Although it is reasonable to suppose that at low pressures this description should be valid, accurate vapor densities at any one temperature are not available over a wide enough range of pressures to establish the point by experiment. Consequently the entropy requires support from other sources. The calculation has therefore been made at a series of temperatures from 25 to 100° and an average value of the heat capacity between these temperatures has been derived and shown to lie between the heat capacities of the related substances ethyl alcohol and acetone. As a further and more direct confirmation an independent value of the entropy is derived from the results of a recent study of the vapor phase ethyl acetate equilibrium.

In a similar study of the nitrogen dioxide-nitrogen tetroxide case Giauque and Kemp[2] concluded that the entropy of dissociation of the dimer could not be evaluated from equilibrium data within several entropy units. This uncertainty would of course be carried in some measure into the entropy of each component. The acetic acid case appears to be more favorable.

Since the publication by MacDougall[3] of vapor densities measured at low pressures near room temperature, it is possible to evaluate the heat of reaction 1 and the composition of the mixture as a function of temperature with a high probable accuracy. From MacDougall's results and those of Fenton and Garner,[4] the heat of dissociation of the dimer becomes

$$\Delta H = 18{,}853 - 9.76T \quad (2)$$

and, for the dissociation constant,

$$\log k = 25.732 - 4120/T - 4.910 \log T. \quad (3)$$

Constants calculated by Eq. (3) show an average deviation of 2.0 percent from MacDougall's mean values. If his point at 25° is left out the deviation decreases to 0.8 percent. Similarly average constants from the Fenton and Garner data are reproduced with a mean deviation of 1.0 percent, or

TABLE I. *Vaporization and association of acetic acid.*

Temp. Deg. C	ΔH Dis.	k (Dis.) mm	p mm	α	ΔH Vap.
25	15,944	0.578	15.63	0.0957	10,874
40	15,797	2.080	34.72	.1215	11,011
60	15,602	9.48	88.96	.1611	11,236
80	15,407	35.8	202.4	.2058	11,497
100	15,212	115.1	417.2	.2540	11,779

[1] The author is indebted to Dr. Donald Brundage for making preliminary calculations.
[2] W. F. Giauque and J. D. Kemp, J. Chem. Phys. **6**, 41 (1938).
[3] MacDougall, J. Am. Chem. Soc. **58**, 2585 (1936).
[4] Fenton and Garner, J. Chem. Soc. p. 694 (1930).

TABLE II. *Entropy of the acetic acid monomer.*

TEMP. DEG. C	S (60 G LIQ.)	ΔH_1	$\Delta H_1/T$	p_1	R LN $760/p_1$	S_1 GAS
25	38.2[0]	12,646	42.4[2]	2.73[1]	11.2[3]	69.3[9]
40	39.6[7]	12,445	39.7[5]	7.52[4]	9.1[7]	70.2[4]
60	41.5[9]	12,162	36.5[1]	24.6[9]	6.8[1]	71.2[9]
80	43.4[5]	11,867	33.6[1]	69.0[8]	4.7[7]	72.2[9]
100	45.2[8]	11,564	30.9[9]	169.0	2.9[9]	73.2[9]

0.3 percent at three of their four temperatures. Results obtained by Drucker and Ullmann[5] at three temperatures from 80 to 110° are on the average 5 percent above the constants given by Eq. (3). If the weight at higher temperatures were given to the Drucker and Ullmann results it would be impossible to bring Eqs. (2) and (3) into line with the remaining data without an unreasonably large ΔC_p term expressed in greater detail. The heat of dissociation according to Eq. (2) is 15,944 cal. at 25° as compared with 16,400±800 obtained by MacDougall from his own data alone. Since it seems apparent that his equilibrium constant at 25° is low, and his mean heat of reaction therefore high, the correct value should lie within the lower half of his range of uncertainty. Equation (2) gives heats of dissociation within these limits up to 60°.

The heat of vaporization is evaluated from the vapor pressures in the *International Critical Tables*,[6] which are reproduced with an average deviation of 0.1 percent from 20 to 100° by the equation

$$\log p = 18.8302 - 2630/T - 3.562 \log T. \quad (4)$$

For the vaporization of 120 grams of the acid

$$\Delta H = (1+\alpha)(12035 - 7.08T). \quad (5)$$

Table I contains the heat of dissociation, the degree of dissociation α, the dissociation constant, the vapor pressure and the heat of vaporization calculated from the above equations at five temperatures. The heats of vaporization listed in the *International Critical Tables*[7] and marked as questionable are as much as 320 cal. lower than those appearing in Table I. MacDougall's values, 11,000 at 25° and 11,270 at 40° are correspondingly high. They cannot be taken as more reliable, however, because they are based upon low pressures measured over a range of only 20°. If gas imperfections have been adequately accounted for in the factor $1+\alpha$, the heats of vaporization derived from Eq. (5) should not be in error by more than 100 calories.

The entropies of vaporization of the monomer and dimer are most readily obtained with the aid of individual heats of vaporization calculated from the equations

$$\Delta H_1 \text{ (vap.)} = \Delta H \text{ (vap.)}/2 + (1-\alpha)\Delta H \text{ (dis.)}/2 \quad (6)$$

and

$$\Delta H_2 \text{ (vap.)} = \Delta H \text{ (vap.)} - \alpha \Delta H \text{ (dis.)}. \quad (7)$$

For 60 grams of liquid the entropy at 25° is 38.2 according to Parks, Kelley and Huffman.[8] The added liquid entropy for higher temperatures is calculated from the heat capacity given in the *International Critical Tables*.[9] After conversion to calories this becomes $C_p = 12.9 + 0.056T$ in the appropriate temperature range. The results of the entropy calculation are shown in Table II for the monomer and in Table III for the dimer. The mean heat capacity of the monomer and dimer vapors is now derived from the entropy by means of the equation $dS/dT = C_p/T$. For the monomer, C_p is 17.4 and for the dimer it is 44.1. Because of structural similarity it is reasonable to assume that the monomer value should be near the mean of the heat capacities of ethyl alcohol and acetone. From Table IV these are, respectively, 16.8 and 19.9 at the mean temperature of 62°. For reaction 1, ΔC_p is -9.3 as compared with -9.76 shown in Eq. (2). This discrepancy is probably due to an oversimplification of Eq. (5), for which the true heat capacity, there represented as $-7.08(1+\alpha)$, should have the more

TABLE III. *Entropy of the acetic acid dimer.*

TEMP. DEG. C	ΔH_2	$\Delta H_2/T$	p_2	R LN $760/p_2$	S_2 GAS
25	9349	31.3[6]	12.90	8.1[0]	99.6[6]
40	9092	29.0[4]	27.20	6.6[2]	101.7[6]
60	8722	26.1[9]	64.27	4.9[1]	104.4[5]
80	8326	23.5[8]	133.3	3.4[6]	107.0[3]
100	7916	21.2[2]	248.2	2.2[2]	109.5[5]

[5] Drucker and Ullmann, Zeits. f. physik. Chemie **74**, 567 (1910).
[6] Vol. 3, p. 218.
[7] Vol. 5, p. 138.
[8] Parks, Kelley and Huffman. J. Am. Chem. Soc. **51**, 1969 (1929).
[9] Vol. 5, p. 114.

detailed form

$$\Delta C_p = 2\alpha C_{p1} + (1-\alpha) C_{p2} + \Delta H \text{ (dis.)}\, d\alpha/dT - 2C_p(1). \quad (8)$$

Since the discrepancy involves only a fraction of an entropy unit, the second approximation required to produce consistency would not be justified by the data used.

The above calculation using individual heats of vaporization is different in form from the method outlined by Giauque and Kemp.[2] Their approach leads to two equations, the one expressing the two unknowns in terms of the entropy of dissociation of the dimer, the other relating them to the entropy of the mixture and the entropy of mixing. The two methods can readily be shown to be equivalent, either by algebraic proof or by numerical substitution.

If the entropy calculation is made from MacDougall's[3] data alone the results for S_1 and S_2 at 25° are 70.3 and 100.0, which represent practical maximum values and show that the entropies are not highly sensitive to the interpretation of the data.

A further estimate of the monomer entropy can be made from the result of a recent study of the vapor phase ethyl acetate equilibrium by Halford and Brundage.[10] For the reaction

$$CH_3COOH(g) + C_2H_5OH(g) = CH_3COOC_2H_5(g) + H_2O(g), \quad (9)$$

the minimum mean value of the entropy reasonably derivable from existing equilibrium data between 40 and 230° is −3.3 units. To derive the value at 25° requires knowledge of the heat capacities of the reactants. Table IV shows estimated values together with references to the data upon which they are based. In the absence of direct data, acetic acid is assumed to have the mean temperature dependence of ethyl alcohol and acetone and the constant term is set to give the value 17.4 at 62° consistent with the entropy calculation. The experimental entropy of reaction 9 is assumed to be correct at the mean temperature of 135° and the entropy of esterification is calculated with the aid of the above heat capacities to be −4.2 at 25°. There is no good basis for estimating the probable error of this value.

TABLE IV. *Heat capacity of gases, 25 to 150°, $C_p = A + BT$.*

	A	B	REFERENCES
H_2O	7.47	0.0017	(a)
C_2H_5OH	3.4	.040	(b)
$CH_3COOC_2H_5$	8.9	.060	(b), (c)
CH_3COOH	5.1	.037	Estimate
CH_3COCH_3	8.5	.034	(b), (c)

[a] A. R. Gordon, J. Chem. Phys. **2**, 65 (1934).
[b] Bennewitz and Rossner, Zeits. f. physik. Chemie **B39**, 134 (1938).
[c] *International Critical Tables*, Vol. 5, p. 79.

[10] J. O. Halford and D. Brundage, in press.

TABLE V. *Entropy of ethyl alcohol, ethyl acetate and acetone at 25°.*

	S LIQ.	ΔH VAP.	p MM	S GAS
Ethyl Alcohol	38.4	10,125	58.6	67.3
Ethyl Acetate	62.0	8,596	93.3	86.7
Acetone	47.8	7,488	229.2	70.6

The entropy of water vapor at 25° and one atmosphere is taken as 45.10.[11,12] For ethyl alcohol, ethyl acetate and acetone the required quantities are summarized in Table V. In the order given the liquid entropies are those of Kelley,[13] Parks, Huffman and Barmore,[14] and Parks, Kelley and Huffman.[8] Both the vapor pressure and the heat of vaporization of the alcohol are values published by Fiock, Ginnings and Holton.[15] Other vapor pressures come from the *International Critical Tables*,[6] and the heats of vaporization are taken from the vapor pressure curves and corrected by means of the equation $PV = RT(1-aP)$, for which a is evaluated from the Mathews[16] heats of vaporization at the respective boiling points. The similarly derived value for the alcohol is 10,150 or 10,195 cal., according to whether the Fiock, Ginnings and Holton heat of vaporization or that of Mathews is taken as correct at the boiling point.

From the entropy of esterification and the results in Table V the entropy of acetic acid at 25° and one atmosphere is estimated to be 68.7. Although this estimate in itself is subject to considerable error, it nevertheless contributes

[11] A. R. Gordon, J. Chem. Phys. **2**, 65 (1934).
[12] Giauque and Stout, J. Am. Chem. Soc. **58**, 1144 (1936); Giauque and Archibald, J. Am. Chem. Soc. **59**, 561 (1937).
[13] Kelley, J. Am. Chem. Soc. **51**, 779 (1929).
[14] Parks, Huffman and Barmore, J. Am. Chem. Soc. **55**, 2733 (1933).
[15] Fiock, Ginnings and Holton, J. Research Nat. Bur. Stand. **6**, 892 (1931).
[16] Mathews, J. Am. Chem. Soc. **48**, 572 (1926).

TABLE VI. *Acetic acid entropy from the entropy of acetone.*

	ACETONE	ACETIC ACID
M	58.08	60.05
ABC	1.48	1.20, 1.23
σ	18	3
I_{CH_3}	0.0527	0.0527
I_{OH}	—	0.0131
S(vib.)	2.4	2.4
S_{298}	70.6	72.7

strongly to the high probability already established that the entropy of the acid monomer lies within the limits 69.4 ± 1.0.

For comparison, a theoretical value is calculated from the entropy of acetone with the aid of the equation

$$S_{298} = 23.730 + (3/2)R \ln M + 8.712n + (1/2)R \ln (A^a B^b \cdots G^g) - R \ln \sigma + S \text{ (vib.)} \quad (10)$$

in which M is the molecular weight in grams, A, B, etc., are moments of inertia, external and internal, in c.g.s. units times 10^{38}, $a+b+\cdots+g=n$ is the number of rotational degrees of freedom and σ is the symmetry number. Equation (10), for the entropy with free internal rotation, differs only negligibly from the theoretically correct form derived by Kassel.[17] It is assumed in its application to acetic acid that the hydroxyl group may be described closely enough as a symmetrical internal rotator. The vibrational entropy of acetone is derived from the total entropy in Table V by the use of the above equation, and should therefore be low by an amount representing the restriction of internal rotation. For acetone the restricting barrier is probably small,[18] corresponding almost to free rotation. Acetic acid is then assumed to have the same vibrational entropy, and its total entropy, shown in Table VI, should therefore be only a little lower than the free rotation value.

This approach, rather than the customary one involving a questionable independent estimate of the vibrational contribution, is of special interest because it can be used to calculate the entropy of methyl alcohol from that of ethane or of ethyl alcohol from propane within a small fraction of an entropy unit. Consequently the result of Table VI is the entropy which acetic acid would have if the substitution of the hydroxyl group for a methyl group produced the same changes in all three molecules, ethane, propane and acetone.

In calculating the external moment product ABC and the moments of inertia I of the internal rotators, all angles between single bonds were assigned the tetrahedral value, and interatomic distances were taken as $c-c=1.54$A, $c-h=1.09$, $c-o=1.43$, $c=o=1.24$ and $o-h=0.97$. For acetic acid the two tabulated moment products were calculated for models with the acid hydrogen in the *cis*- and *trans*-positions relative to the carbonyl oxygen. The hydroxyl group was assumed to rotate as if its center of gravity were on the C–O bond.

It appears from the above results that restricted rotation of the acid hydroxyl group causes an entropy decrease below the free rotation value which exceeds the corresponding effect in methyl or ethyl alcohol by nearly three units. This large deficiency can be readily explained in a way that indicates that the experimental entropy of 69.4 is not far from correct. It is reasonable to assume that in the entire rotational cycle there is only a single potential minimum of sufficient depth to trap the hydroxyl group. For such a model, with vibration restricted to the ground state, the entropy would be 68.3 plus a small increment entering through the use of the acetone vibrational entropy. The experimental value thus allows 1.1 e.u. to be divided between this increment and the actual entropy of the torsional motion.

Although Pitzer's[19] method of finding the restricting potential barrier was developed for n equal sinusoidal potential valleys each covering one nth of the cycle, his table can be used for the single minimum model postulated for acetic acid. The case is similar to his treatment of the individual forms of n-butane.[20] It is assumed that the single minimum occupies one-third of the cycle. For an imaginary model with two more minima equal in depth to the first the entropy would be 69.4 plus a mixing term $R \ln 3$, giving $S_f - S = 1.1$ for use in the table. The resulting potential barrier is about 3000 cal., a value which

[17] L. S. Kassel, J. Chem. Phys. **4**, 276 (1936).
[18] S. C. Schumann and J. G. Aston, J. Chem. Phys. **6**, 485 (1938).
[19] K. S. Pitzer, J. Chem. Phys. **5**, 469 (1937).
[20] K. S. Pitzer, J. Chem. Phys. **5**, 473 (1937).

is subject to an error, probably negligible, because the table applies only when the rotational states are symmetrically disturbed in n regions of the cycle, rather than unsymmetrically as they would be in the single minimum case.

In general, for the hydroxyl group in torsional motion against an unsymmetrical radical, it will be necessary to add a mixing term to the experimental entropy before a potential barrier can be estimated by means of Pitzer's table or the equivalent functions. This term has a maximum value $R \ln n$, but may be near zero if the potential valleys approach equality in depth. With ethyl alcohol, for example, there are probably three minima of which two are equal but different from the third, and a mixing term between zero and $R \ln 3$ should be added to the experimental entropy before the barrier is estimated. If the correction is not made the barrier will be high.

An interesting possibility occurs for substances which have stable torsional vibrations resulting in optically isomeric configurations. The molecules might remain asymmetric after crystallization and might produce crystals of the racemic compound type which would remain unchanged upon cooling toward the absolute zero. Consequently the entropy at the absolute zero would not be zero but $R \ln 2$, and the third law entropy would be in error by this amount. How probable this situation is depends upon the relative magnitude of intramolecular and intermolecular forces in the solid state.

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Second Virial Coefficients of Polar Gas Mixtures‡

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An empirical equation used by Keyes to represent the second virial coefficients of several polar gases is compared to a theoretical expression for the same quantity. The constants appearing in this equation are discussed in terms of intermolecular forces, and their relationship to analogous constants in the Beattie-Bridgeman equation for non-polar gases is examined. These considerations permit the construction of simple rules by means of which the second virial coefficient of any gas mixture may be calculated if the second virial coefficients and dipole moments of the pure component gases are known. The success of these rules is demonstrated by comparison with data on H_2O-CO_2, N_2-NH_3, and N_2-H_2O systems. In the case of N_2-H_2O mixtures (vapor-liquid equilibrium data) the agreement is not satisfactory at the higher temperatures. A rough method of including the effect of higher virial coefficients reduces, but does not remove, this discrepancy.

INTRODUCTION

THE Beattie-Bridgeman equation of state for gas mixtures[1] has been applied successfully not only to the calculation of the compressibility of many gas mixtures, but also to the correlation of several types of high pressure equilibrium data.[2] A substance conspicuously absent from all these calculations is steam, for the reason that the experimental $p-V-T$ data[3] cannot be adequately represented by an equation of the Beattie-Bridgeman form. The curvature of the isometric lines for steam is so great that the ordinary Beattie-Bridgeman function is unsatisfactory. Theoretically this great curvature may be shown to be a direct consequence of the nature of the forces between highly polar mole-

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[1] J. A. Beattie, J. Am. Chem. Soc. **51**, 19 (1929); J. A. Beattie and S. Ikehara, Proc. Am. Acad. **64**, 127 (1930).

[2] L. J. Gillespie, Chem. Rev. **18**, 359 (1936), where a complete list of references to important earlier work is given. See especially Gillespie, J. Am. Chem. Soc. **47**, 305 and 3106 (1925); Gillespie and Beattie, Phys. Rev. **36**, 743, 1008 (1930).

[3] F. G. Keyes, L. B. Smith, and H. T. Gerry, Proc. Am. Acad. **70**, 319 (1936).

cules, so that the Beattie Bridgeman equation might also be expected to fail for other highly polar substances, although it seems to be adequate for ammonia.[4] Since equilibria involving the vapor phase of water, alcohols, and other highly polar substances are of some interest, the development of an equation of state suitable for mixtures containing components of this nature seems desirable.

Interpretation of Empirical Equations

The second virial coefficient $B(T)$ is defined in either of the two virial expansions:

$$pv/RT=1+B/v+C/v^2+\cdots, \quad (1)$$

$$pv=RT+Bp+C'p^2+\cdots, \quad (2)$$

where v is the molal volume. In the Beattie-Bridgeman equation of state, B takes the form

$$B(T)=B_0-A_0/RT-c/T^3. \quad (3)$$

By proper choice of the three disposable constants, this function can be used to represent quite accurately the experimental second virial coefficients of all non-polar gases up to temperatures well above the Boyle temperature. For steam, however, it has already been mentioned that Eq. (3) is inadequate. Keyes, Smith, and Gerry[3] found that the data for steam could be reproduced accurately by an equation of the form

$$B(T)=B_0-(A/RT)\exp(D/T^2). \quad (4)$$

Keyes[5] has also found that this function is superior to Eq. (3) in representing the data for ammonia.

Expansion of the exponential in Eq. (4) reveals that there is a close relationship between Eq. (3) and Eq. (4), and in fact the two equations become practically indistinguishable when they are applied to non-polar gases.[6] We shall therefore regard Eq. (4) as a general empirical equation applicable to all types of pure gases, and shall proceed to consider its application to a general gas mixture. The tedium of a purely empirical approach to the last-named problem can be considerably reduced if the constants B_0, A, and D can be given at least an approximate theoretical significance, for then the existing theory of intermolecular forces may be used as a guide. We therefore turn to an examination of Eq. (4) from this point of view.

Recently an equation for the second virial coefficient of a polar gas[7] was derived on the assumption that the intermolecular potential energy could be written in the somewhat idealized form

$$U=\lambda r^{-s}-\kappa r^{-6}-\mu^2 r^{-3}g, \quad (5)$$
$$g=2\cos\theta_1\cos\theta_2-\sin\theta_1\sin\theta_2\cos\varphi,$$

where μ is the permanent dipole moment and θ_1, θ_2, φ specify the orientation. The term $-\kappa r^{-6}$ in Eq. (5) is taken to include both dispersion and induction effects (the latter being always small). It was demonstrated that the equation so derived could be fitted closely to the data for steam and ammonia, and the values of κ thus obtained were in good agreement with those predicted by quantum theory. It was also found that the error inherent in the assumption of classical statistics, as calculated from the theory of Kirkwood,[8] was practically negligible.

For the present purpose it is sufficient to consider only the result obtained in the special case that the exponent s in the repulsive energy of Eq. (5) is allowed to become very large. The potential energy then becomes

$$\begin{aligned} U&\to\infty && (r<\sigma),\\ &=-\kappa r^{-6}-\mu^2 r^{-3}g && (r\geqslant\sigma), \end{aligned} \quad (6)$$

and the second virial coefficient is given by

$$B(T)=(2\pi N\sigma^3/3)\Big[1-\sum_{n=1}^{\infty}\sum_{m=0}^{m\leq n/2}Q_{nm}\times(\kappa/\sigma^6kT)^n(\mu^2\sigma^3/\kappa)^{2m}\Big]. \quad (7)$$

where N is Avogadro's number, k is Boltzmann's constant and the coefficient Q_{nm} are numbers whose definition[7] need not be repeated here.

The relation of Eq. (7) to the empirical Eq. (4) must now be examined. Let a function

[4] J. A. Beattie and C. K. Lawrence, J. Am. Chem. Soc. **52**, 6 (1930).

[5] F. G. Keyes, J. Am. Chem. Soc. **60**, 1761 (1938).

[6] This condition requires that the quantity Rc/A_0T^2 be sufficiently small. For n-butane [J. A. Beattie, G. L. Simard, and G. J. Su, J. Am. Chem. Soc. **61**, 26 (1939)], Rc/A_0 has the value 1.62×10^4, which is larger than that for almost all other non-polar gases. Yet at 400°K, which is well below the critical temperature, Rc/A_0T^2 is 0.10, and $(A_0/RT)\exp(Rc/A_0T^2)$ is very nearly equal to $(A_0/RT+c/T^3)$.

[7] W. H. Stockmayer, J. Chem. Phys. **9**, 398 (1941). The exponent of y in Eq. (5) of this reference was incorrectly printed, and should read $(ns-6n+6k)/s$.

[8] J. G. Kirkwood, J. Chem. Phys. **1**, 597 (1933).

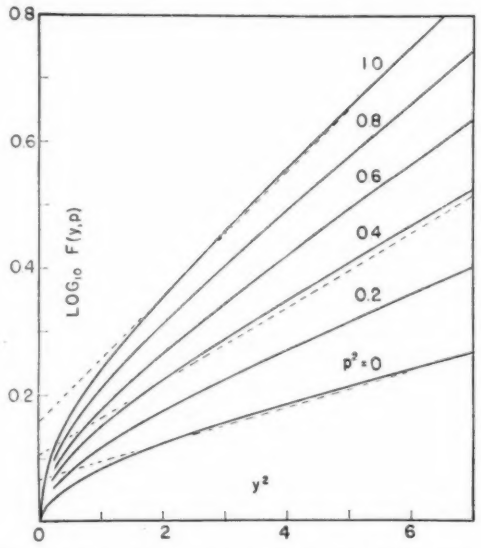

FIG. 1. A function related to the theoretical second virial coefficient of a polar gas. Full lines, Eq. (9). Dotted lines, Eq. (10).

$F(y, p)$ be defined by the equation

$$B(T)=(2\pi N\sigma^3/3)[1-yF(y, p)], \tag{8}$$

where

$$y=\kappa/\sigma^6kT,$$

and

$$p=\mu^2\sigma^3/\kappa.$$

Then, according to Eq. (7),

$$F(y, p)=\sum_{n=1}^{\infty}\sum_{m=0}^{m\leq n/2}Q_{nm}y^{n-1}p^{2m}. \tag{9}$$

If now the theoretical Eq. (7) is in accord with the successful empirical Eq. (4), the logarithm of $F(y, p)$, at a constant value of p, should be a linear function of y^2, since y is proportional to $1/T$. In Fig. 1 are shown plots of log $F(y, p)$, as calculated from Eq. (9), against y^2, at round values of p^2 from 0 to 1. It will be observed that for sufficiently high values of y (i.e., sufficiently low temperatures), this condition is fulfilled rather well. The temperatures for which it is invalid are fortunately above the domain of experiment for the known polar gases. A further study of $F(y, p)$ reveals that the slope of the straight-line portion of the curve is approximately a linear function of p^2. It is found that the logarithm of the intercept of the extrapolated straight-line portion on the log F axis is also linear in p^2. More concisely, for $y>1.3$ the theoretical function can be approximated by means of the simple formula

$$F(y, p)=(1.160+0.282p^2)\times\exp(0.067y^2+0.159p^2y^2). \tag{10}$$

The dotted lines of Fig. 1 were calculated from this expression. A comparison of this result with Eq. (4) reveals that the empirical constants B_0, A, and D may be related to the parameters σ, κ, and μ of the intermolecular energy. It becomes possible to write each of the constants A and D as a sum of two terms, the one depending only on κ and σ (and therefore only on the type of intermolecular force common to *all* kinds of molecules), and the other depending on μ (and differing from zero only if the molecules are polar). We thus write simply

$$A=A_0+A_p, \quad D=D_0+D_p. \tag{11}$$

After introduction of the approximate numerical expression for $F(y, p)$ given in Eq. (10), it is found that

$$\begin{aligned} B_0&=2\pi N\sigma^3/3,\\ A_0/RB_0&=1.16\kappa/\sigma^6k,\\ A_p/RB_0&=0.282\mu^4/\kappa k,\\ D_0&=0.067(\kappa/\sigma^6k)^2,\\ D_p&=0.159(\mu^2/\sigma^3k)^2. \end{aligned} \tag{12}$$

These equations give at least a rough interpretation of the empirical constants, adequate for present purposes.

Since only A and D, and not their component parts, are determined by fitting Eq. (4) to experimental data, a knowledge of one other parameter, such as μ, is required before A_0, A_p, D_0, and D_p can be calculated separately. Manipulation of Eqs. (11) and (12) yields the relations[9]

$$\begin{aligned} A_0&=\tfrac{1}{2}[A+(A^2-0.756\mu^4)^{\frac{1}{2}}],\\ A_p&=\tfrac{1}{2}[A-(A^2-0.756\mu^4)^{\frac{1}{2}}],\\ D_0&=0.048(A_0/RB_0)^2,\\ \text{or } D_p&=13.6\mu^4/B_0^2, \end{aligned} \tag{13}$$

when A and A_0 are in liters^2—atmos./mole^2, B_0 is in liters/mole, and μ is in Debye units (10^{-18} e.s.u.). The two alternative methods of splitting

[9] It is interesting to note that this method gives $D_0=0.048(A_0/RB_0)^2$, while Keyes, reference 5, chose $Rc/A_0=0.023(A_0/RB_0)^2$ from a corresponding states study of the experimental Beattie-Bridgeman constants for non-polar gases. The number 0.024 was obtained by Hirschfelder and Roseveare [J. Chem. Phys. **43**, 15 (1939)] via the Lennard-Jones (12, 6) potential energy function. The discrepancy is not annoying, since the rule is only very approximate. Actually, many gases yield numbers closer to 0.048 than to the other values.

D into D_0 and D_p, given by the last two lines in Eq. (13), generally do not yield identical results, since their derivation depends on the use of the inexact intermolecular potential energy of Eq. (6); on the other hand, the disagreement between the two methods is not serious. In the numerical work reported here, D_p was calculated by the last line in Eq. (13), and D_0 was then found by difference from Eq. (11). The constants derived by this method for ammonia and steam are given in Table I. It is to be noticed that for both these gases the non-polar contribution to A is by far the largest, while the dominance of the dipole forces in D (which determines the curvature of the isometrics) is especially striking in the case of steam.

Combining Rules for Mixtures

The second virial coefficient of a gas mixture depends on the composition in accordance with the equation

$$B=\sum_i \sum_j x_i x_j B_{ij}, \tag{14}$$

where x_i, x_j are mole fractions and the sums go over all species present. Each of the quantities B_{ij} is a function only of temperature, and the terms for which $i \neq j$ depend on the force between a pair of unlike molecules. The aim of an equation of state for mixtures is to express the quantities B_{ij} (and their analogues in the higher virial coefficients) in terms of the properties of the pure gases, in the most favorable case from a knowledge of B_{ii} and B_{jj} alone.

A semi-empirical treatment of this nature has been developed for the Beattie-Bridgeman equation[1] for non-polar gases, and has also been employed successfully for the Keyes[10] equation of state. For the second virial coefficient, as given by Eq. (3), the most successful set of rules[11] is that expressed below:

$$\begin{aligned}(B_0)_{ij}&=\tfrac{1}{8}(B_{0ii}^{1/3}+B_{0jj}^{1/3})^3,\\ (A_0)_{ij}&=(A_{0ii}A_{0jj})^{\frac{1}{2}},\\ c_{ij}&=(c_{ii}c_{jj})^{\frac{1}{2}}.\end{aligned} \tag{15}$$

For the majority of gases B_0 is of the same order of magnitude, so that a simpler rule is often adequate:

$$(B_0)_{ij}=\tfrac{1}{2}(B_{0ii}+B_{0jj}).$$

It is not difficult to give rough theoretical reasons for the success of Eqs. (15). The rule for B_0 was first given by Lorentz[12] for its analogue b in the van der Waals equation, and follows from the assumption that the collision radii of the two unlike molecules may be added to obtain the collision diameter for the pair. The rules for A_0 and c (and the similar rule which therefore applies to D_0, since for non-polar gases $Rc/A_0 \cong D_0$) follow from the theoretical prediction[13] that the constant κ in the dispersion energy between the unlike pair is not far from (actually, never greater than) the geometric mean of that for the two similar pairs. It is true that Eq. (12) shows A_0 to be proportional to κ/σ^3, and D_0 proportional to $(\kappa/\sigma^6)^2$, but any alternatives are only equally speculative and more cumbersome. Furthermore, the values of σ do not vary greatly from gas to gas. Since Eq. (4) reduces essentially to Eq. (3) when the gases are non-polar, so that $D_0=Rc/A_0$, the rules given by Eq. (15) may be retained for B_0, A_0, and D_0 in the general case.

Without the theoretical analysis of A and D, it might have seemed natural merely to apply square-root combination rules directly to A and D, in view of the apparent similarity of Eqs. (3) and (4). It has been demonstrated, however, that a significant portion of each of these constants is due to the dipole-dipole forces, which vanish when one of the molecules in a pair is non-polar. It would therefore be expected that such a simple procedure would considerably overestimate the attractive force between a polar and a non-polar molecule, and cause values of B_{ij} thus calculated to be algebraically too low. It

Table I. *Constants of Eq. (4) for the second virial coefficients of steam and ammonia.*

Quantity	H_2O[a]	NH_3[b]
B_0 (liter/mole)	0.03405	0.04087
A (liter²—atmos./mole²)	3.905	3.237
D (°K^{-2})	18.58×10^4	7.744×10^4
μ (Debye units)	1.83	1.47
A_0	3.254	2.936
A_p	0.651	0.301
D_0	5.42×10^4	3.943×10^4
D_p	13.16×10^4	3.801×10^4

[a] Reference 3 in text. [b] Reference 5 in text.

[10] F. G. Keyes and H. G. Burks, J. Am. Chem. Soc. **50**, 1100 (1927); L. J. Gillespie, Proc. Nat. Acad. Sci. **11**, 73 (1925).

[11] J. A. Beattie, W. H. Stockmayer, and H. G. Ingersoll, J. Chem. Phys., this issue, following article.

[12] H. A. Lorentz, Ann. de Physik. **12**, 127, 660 (1881).

[13] F. London, Zeits. f. physik. Chemie. **B11**, 222 (1930).

will be seen later that comparisons with experimental data verify this prediction. The theoretical treatment shows that actually A and D for the pure gases must be split up into their components A_0, A_p, D_0, D_p, and separate rules must be devised for each of these constants. Since Table I shows A to be mostly the result of the dispersion forces the error in A_{ij} would not be serious, but for D_{ij} the two procedures yield vastly different results.

Rules for A_p and D_p are easy to construct, since the results of the previous section carry over for a pair of dissimilar polar molecules if μ^2 is simply replaced by $\mu_i\mu_j$. Hence the geometric mean rule is also suggested for these two constants. The complete set of rules thus suggested by theory is given below:

$$\begin{aligned}(B_0)_{ij}&=\tfrac{1}{8}(B_{0ii}^{1/3}+B_{0jj}^{1/3})^3,\\ (A_0)_{ij}&=(A_{0ii}A_{0jj})^{\frac{1}{2}},\\ (A_p)_{ij}&=(A_{pii}A_{pjj})^{\frac{1}{2}},\\ (D_0)_{ij}&=(D_{0ii}D_{0jj})^{\frac{1}{2}},\\ (D_p)_{ij}&=(D_{pii}D_{pjj})^{\frac{1}{2}},\end{aligned} \qquad (16)$$

where $D_0=Rc/A_0$ for non-polar gases.

It is thus possible, by means of Eqs. (13), (14), and (16), to calculate the second virial coefficient of any gas mixture as a function of temperature and composition, if the constants in Eqs. (3) or (4), and the dipole moments, are known for each of the pure substances involved.

Applications

The simplest and most direct test of the rules just derived is afforded by some unpublished data of L. J. Gillespie and H. T. Gerry,[14] who determined, at several temperatures, the increase in pressure when a small measured amount of water is injected into a thermostated bomb containing a known quantity of carbon dioxide. The range of CO_2 pressure in these experiments was 1 to 15 atmospheres. If subscript 1 refers to H_2O, 2 to CO_2, the pressure increase is given by

$$\Delta p=(n_1RT/V)(1+2n_2B_{12}/V)+n_1^2B_{11}RT/V^2+\cdots, \qquad (17)$$

where the n's are mole numbers and V is the total volume of the bomb. At 50°C the data are rather erratic, but at 70° and 90°, although there is some evidence of adsorption on the walls of the bomb, they are very consistent. The quantity B_{12} is determined from these experiments probably to within 5 or 10 cc/mole. In Table II is presented a comparison of Gillespie and Gerry's observed values of B_{12} with those calculated by several methods. The column headed "old rules" refers to the method of applying square-root combination, not separately to A_0, A_p, D_0, D_p, but to A and D directly. The column headed "new rules" gives the result of calculations by the methods derived in this paper. The constants used for CO_2 were taken from Beattie and Bridgeman,[15] and those for H_2O have been given in Table I. The dipole moment of CO_2 is, of course, taken to be zero. Table II shows that the new rules lead to values of B_{12} which are above the observed by about 10 cc/mole, which may be within the experimental error. They are far superior to the older rules, which give an error of from three to four times this amount in the opposite direction, as was predicted.

TABLE II. *Interaction term, B_{12}, for the second virial coefficient of H_2O-CO_2 mixtures.* (Units: liters per mole.)

t (°C)	Obs.[a]	Calc. Old Rules	Calc. New Rules
50	$\left\{\begin{matrix}-0.120\\-0.149\end{matrix}\right\}$	−0.193	−0.129
70	−0.123	−0.167	−0.112
90	−0.111	−0.146	−0.100

[a] Reference 14 in text.

Another experiment by means of which these rules may be tested is that of Lurie and Gillespie,[16] who measured the total pressure and composition of N_2-NH_3 mixtures in equilibrium with solid $BaCl_2\cdot 8NH_3$ at 45°C. The accuracy of the data is not sufficient to justify a detailed comparison. By use of the Beattie-Bridgeman equation for nitrogen[15] and the Keyes expression for the second virial coefficient of ammonia,[5] (see Table I) the mole fraction of ammonia in the gas is calculated to be 0.152 when the total pressure is 60 atmospheres. The measured value is 0.148. For this experiment, however, equal success is obtained by using the Beattie-Bridgeman equation for ammonia[4] and the ordinary combining

[14] H. T. Gerry, Ph.D. Thesis, Massachusetts Institute of Technology (1932).

[15] J. A. Beattie and O. C. Bridgeman, Proc. Am. Acad. **63**, 229 (1928).

[16] E. Lurie and L. J. Gillespie, J. Am. Chem. Soc. **49**, 1146 (1927).

TABLE III. N_2-H_2O *vapor-liquid equilibrium at 100 atmos.* x_1 *= mole fraction of* H_2O *in vapor.*

t (°C)	x_1 (OBS.)[a]	p_e/P	CALC. EQ. (21)	CALC. EQ. (25)
50	0.00183	0.00130	0.00185	0.00183
80	0.00626	0.00498	0.00661	0.00651
100	0.0113	0.0106	0.0136	0.0134
150	0.0520	0.0495	0.0604	0.0593
190	0.123	0.130	0.155	0.150
230	0.275	0.286	0.332	0.318

[a] Reference 17 in text.

rules for non-polar gases, in which gas the calculated mole fraction is 0.151. Undoubtedly compensation of errors occurs here, for the Keyes expression gives a much better representation of the experimental second virial coefficients of NH_3. The results of this calculation, while further substantiating the new rules, show that, in some cases, less involved methods may be equally satisfactory. It should also be remarked that for this calculation the equation of state was considered to terminate at the second virial coefficient. It is conceivable that inclusion of higher terms could have a small effect on the result.

A very stringent test of the methods developed in this paper is in their application to vapor-liquid equilibrium in the system N_2-H_2O, for which Saddington and Krase[17] have measured both liquid and vapor compositions from 50°C to 230°C and at 100, 200, and 300 atmospheres total pressure.

The necessary thermodynamic equations have been adequately discussed previously,[2] so that they are merely stated here. Let subscript 1 refer to H_2O and subscript 2 to nitrogen, let P be the total pressure, p_0 the vapor pressure of water, v_1 the molal volume of H_2O vapor, V the total volume of the gas mixture, x_1 the mole fraction of H_2O in the vapor, y_1 its mole fraction in the liquid, and $\bar{v}_L$ the partial molal volume of H_2O in the liquid. Then

$$RT \ln \frac{Px_1}{p_e} = \int_0^{p_e} \left[v_1 - \frac{RT}{p} \right] dp - \int_0^P \left[\frac{\partial V}{\partial n_1} - \frac{RT}{p} \right] dp, \quad (18)$$

where p_e is to be calculated from the equation

$$\int_{p_0}^P \bar{v}_L dp = RT \ln \frac{p_e}{p_0 y_1} + \int_{p_0}^{p_e} \left[v_1 - \frac{RT}{p} \right] dp. \quad (19)$$

Eq. (19) contains the implicit assumption that Raoult's law describes the dependence of p_e on the liquid composition, which is certainly justified, since the mole fraction of water in the liquid is always very nearly unity. The calculation of p_e can be simplified by taking $\bar{v}_L$ as equal to the molal volume v_L of pure water at the mean pressure $(P+p_0)/2$. It was also found that the integral in the second equation could be neglected, so that p_e was computed from the simple equation

$$v_L(P-p_0) = RT \ln (p_e/p_0 y_1). \quad (20)$$

If the equations of state of both pure water vapor and of the gas mixture terminate at the second virial coefficient, Eq. (18) becomes

$$RT \ln \frac{Px_1}{p_e} = -B_{11}(P-p_e) - P(1-x_1)^2 \times (2B_{12}-B_{11}-B_{22}), \quad (21)$$

which is the equation used for the calculations presented in the fourth column of Table III. Values of y_1 were taken from Saddington and Krase,[17] while p_0, v_L, and B_{11} were obtained from the data of Smith, Keyes, and Gerry.[3,18] The B_{22} values (for N_2) are calculated from the Beattie-Bridgeman equation,[15] and B_{12} was obtained from B_{11} and B_{22} by means of Eqs. (13), (14), and (16). The fourth column of Table III shows that the calculated value of x_1 at 100 atmospheres is in remarkable agreement with the measured value at 50°C, but that at higher temperatures the error becomes serious. The third column shows, in fact, that the simple form of Dalton's law, $x_1 = p_e/P$, gives better results at high temperatures.

If square-root combination rules are applied to A and D, instead of to A_0, D_0, A_p, and D_p separately, the calculated mole fractions are considerably higher, and thus in even poorer agreement with experiment. However, in order to prove definitely that this state of affairs is not due to cancelation of errors, the effect of including higher virial coefficients in the equation

[17] A. W. Saddington and N. W. Krase, J. Am. Chem. Soc. **56**, 353 (1934).

[18] F. G. Keyes, L. B. Smith, and H. T. Gerry, Proc. Am. Acad. **69**, 137, 285 (1934).

of state should be investigated. The first integral of Eq. (18) presents no difficulty, for this refers to pure steam, and the complete equation of Keyes, Smith, and Gerry[3] may be used. The term involving the gas mixture is not so simple, and the following procedure is admittedly very approximate.

The third virial coefficient C of Eq. (1), which is related to the coefficient C' in Eq. (2) by the identity $RTC'=C-B^2$, depends on composition, in a binary mixture, according to the equation

$$C_{\text{mix}}=x_1^3C_{111}+3x_1^2x_2C_{112}+3x_1x_2^2C_{122}+x_2^3C_{222}. \quad (22)$$

In the experiments under discussion the mole fraction of nitrogen is always much larger than that of H_2O, so that (except perhaps at the two highest experimental temperatures) the terms in C_{122} and C_{222} are all that need be considered, even after the differentiation indicated in Eq. (18) is performed. The quantity C_{222} can be calculated at once from the Beattie-Bridgeman equation for nitrogen,[15] but the term C_{122} is related theoretically to ternary clusters in which a pair of N_2 molecules interacts with a single H_2O molecule, and it cannot be accurately evaluated in any simple way. It is fortunate that only one water molecule is involved in this term, so that the dispersion forces alone need be considered. If it be assumed that C_{122} is not very different from a similar quantity corresponding to the encounter of three identical molecules, each pair of which interacts with an energy equal to that between a nitrogen molecule and a water molecule, the law of corresponding states, which holds fairly well for non-polar gases, can be applied. Corner[19] has recently discussed the third virial coefficient of the Beattie-Bridgeman equation from this point of view. According to this equation, the third virial coefficient C for a pure gas is given by

$$C=-B_0b+A_0a/RT-B_0c/T^3, \quad (23)$$

where b and a are the two additional constants in the Beattie-Bridgeman equation, and the law of corresponding states implies that the dimensionless ratios b/B_0 and a/B_0 should not differ greatly from gas to gas.[19] The quantity C_{122} was therefore calculated from Eq. (23) with the use of the constants $(B_0)_{12}$, $(A_0)_{12}$, and c_{12} (which equals $(A_0)_{12}(D_0)_{12}/R$), as calculated from Eq. (16), and the same ratios of $a_{12}/(B_0)_{12}$ and $b_{12}/(B_0)_{12}$ as are found for a/B_0 and b/B_0 in the Beattie-Bridgeman equation for pure nitrogen.[15] It is found in this manner that C_{122} differs only trivially from C_{222}, so that the artifice employed in the calculation cannot lead to much error in this particular case. Such a result might have been expected, since the dispersion force between a nitrogen molecule and a water molecule is not very different from that between two nitrogen molecules. Thus the limiting value (at small mole fractions of water vapor) of the contribution of the third virial coefficient to the integral of Eq. (18) involving the gas mixture can be evaluated. The differentiation yields

$$\lim_{x_1\to 0}\frac{\partial}{\partial n_1}[(n_1+n_2)C'_{\text{mix}}] =(3C_{122}-2C_{222}-4B_{12}B_{22}+3B_{22}^2)/RT, \quad (24)$$

If this term is designated by E, an approximation (for small x_1) to the true form of Eq. (18) may be written

$$RT\ln(Px_1/p_e)=-B_{11}(P-p_e)-C_1'p_e^2/2-EP^2/2-P(1-x_1)^2(2B_{12}-B_{11}-B_{22}), \quad (25)$$

where C_1' is the third virial coefficient (in the pressure expansion) of pure steam, as defined by Eq. (2). The mole fractions calculated with Eq. (25) are shown in the last column of Table III. The improvement over Eq. (21) is not great, but this calculation at least indicates that the alternative rules are inferior, since the calculated values are still too high, except at 50°C. Undoubtedly a more exact treatment of the third (and perhaps higher) virial coefficients, if this were possible, would further reduce the discrepancy. More experimental work on this system, at total pressures of twenty atmospheres or less, would be very desirable, since at such

TABLE IV. N_2-H_2O *vapor-liquid equilibrium at higher pressures.*

P (Atmos.)	t (°C)	x_1 (Obs.)	p_e/P	Eq. (25)
300	50	0.00114[a]	0.00050	0.00132
300	230	0.138[a]	0.107	0.146
1000	50	0.00049[b]	0.00024	0.0039

[a] Reference 17 in text.
[b] Reference 20 in text.

[19] J. Corner, Trans. Faraday Soc. **37**, 358 (1941).

pressures the contribution of the higher virial coefficients is much less important.

It is instructive, nevertheless, to see how good an approximation is given by Eq. (25) at even higher pressures. A few calculations are summarized in Table IV. The agreement is good at 300 atmospheres, and, as at 100 atmospheres, Dalton's law gives fairly good results at higher temperatures. The point at 1000 atmospheres was observed by Bartlett,[20] whose results at 100 to 300 atmospheres are below those of Saddington and Krase by thirty or forty percent. Since the latter authors took special pains to avoid premature condensation of water vapor in the expanded gas mixture, their data are possibly more reliable, so that the serious disagreement at 1000 atmospheres may not be as bad as it appears. Furthermore, it is certain that at this high pressure still more terms in the virial expansion should be included. At any rate, it is seen that good results can be obtained with Eq. (25) at 300 atmospheres.

The Lewis and Randall rule[21] is unsatisfactory in this case, for it requires an extrapolation of the equation of state of steam to a pressure far in excess of the vapor pressure. From another point of view, the Lewis and Randall rule implies[2] that the gas mixture obeys Amagat's law; it therefore requires that $2B_{12}$ be equal to $(B_{11}+B_{22})$, and consequently overestimates the attraction between unlike molecules in every case. If Amagat's law is applied to the gas mixture treated here, the calculated mole fractions are too large by about a factor of ten at the lower temperatures. Its success in the treatment of many homogeneous gaseous equilibria[2] may be attributed to cancelation of errors, since differences of chemical potential between products and reactants are then involved. Conversely, the data which have been chosen for examination in this paper furnish much more exacting tests of combining rules than homogeneous equilibrium measurements. They are also superior for this purpose to measurements of the compressibility of gaseous mixtures, for the quantity required is not simply the second virial coefficient of the mixture, but its derivative with respect to the composition.

[20] E. P. Bartlett, J. Am. Chem. Soc. **49**, 65 (1927).
[21] G. N. Lewis and M. Randall, *Thermodynamics* (McGraw-Hill, 1923), Chapter 19.

A calculation by van Laar,[22] although not based on modern theory, agrees well with Bartlett's experiment at 1000 atmospheres. Gillespie,[2] however, has pointed out that van Laar's method is not consistent, for the quantity a in his equations is at one point considered to be independent of pressure, and subsequently to be a function of pressure. Furthermore, from the practical point of view, his calculations are as lengthy as those required by Eq. (25).

Since the inexact introduction of higher virial coefficients into the equation has not resulted in completely satisfactory agreement with experiment, the possibility remains that the combining rules suggested in this paper still lead to a considerable overestimation of the attractive force between a polar and a non-polar molecule, at least when the polar substance is steam. But it must be remembered that these rules were derived from a theory for molecules carrying point-dipoles, and this model is known to be inadequate for a description of the condensed phases of water, or even the gas phases of such substances as hydrogen fluoride or the carboxylic acids. For these substances the hydrogen-bond picture is much more satisfactory, so that water vapor might be regarded as a transition case. In the absence of treatments based on the hydrogen-bond model, however, the proposed rules probably represent the best approximation that can be made at present. The rules should be adequate to deal with the alcohols, for although their dipole moments are quite large their molecular diameters are somewhat greater than that of the water molecule.

The success of Dalton's law for the N_2-H_2O system is obviously due to the compensation of several opposing factors. That it should hold so well is perhaps fortunate, for it means that the simplest possible calculation of the normal dissociation pressures of salt hydrates from gas-steam experiments is also a very nearly correct one. If the proposed combining rules are assumed to be exact, then at 25°C and a total pressure of one atmosphere the dissociation pressures thus calculated will be in error by less than half a percent, while the Lewis and Randall rule may lead to as much as three or four percent error.

The author is indebted to Professor J. A. Beattie for his interest and criticism.

[22] J. J. van Laar, Zeits. f. physik. Chemie **A145**, 207 (1929).

The Compressibilities of Gaseous Mixtures of Methane and Normal Butane. The Equation of State for Gas Mixtures*

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The compressibilities of three gaseous mixtures of methane and normal butane have been measured from 100° to 300°C and from 1.25 to 10 mole/liter (maximum pressure 350 atmos.). The data on these three systems and the two pure hydrocarbons are used to study several methods of combination of constants in the Beattie-Bridgeman equation of state extended to apply to gas mixtures. The best results were obtained with square-root combination for A_0 and for c and Lorentz combination for B_0; but square root combination for A_0 and linear combination for B_0 and for c are a fair compromise between accuracy of representation of the data on mixtures and simplicity of expression.

THE most general method of treating the thermodynamic properties of gas mixtures is by means of an equation of state for gas mixtures. If such an equation is discovered and if it reproduces the trends of the compressibility of mixtures when density, temperature, and composition are varied, then by use of general relations already published[1] it is possible to describe all of the thermodynamic properties of gas mixtures.

The solution of the problem of the equation of state of mixtures requires: (1) an equation for pure gases, and (2) a method of combination of constants for computing the values of the parameters of the mixture from the constants of the pure gases and the composition. An equation for pure gases which employs 5 parameters and represents the compressibility fairly well to the critical density has been published,[2] and lately one having three additional constants and representing the compressibility to twice the critical density has been produced.[3] A study of various methods of combination of constants in the Keyes and the Beattie-Bridgeman equations of state indicates[4] that the properties of mixtures can be reproduced by an equation of state for mixtures almost as well as the equation represents the properties of the pure gases.

Interest in the properties of hydrocarbons is heightened at the present time because of the industrial use of mixtures at high pressures. Besides a large amount of data on liquid-vapor equilibria of mixtures of hydrocarbons the compressibilities of several gaseous mixtures have been measured,[5] in most instances below 125°C. We have measured the compressibility of three gaseous mixtures of methane and *n*-butane from 100° to 300°C and to 10 mole/liter (350 atmos.).

Methane containing a small percentage of nitrogen was obtained from the Southern California Gas Company through the courtesy of Dr. B. H. Sage and Dr. M. Benedict; and methane and *n*-butane of exceptional purity were obtained from the Buffalo Laboratory of the Linde Air Products Company through the courtesy of Dr. L. I. Dana. The *n*-butane was from the same

* Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 490.

[1] L. J. Gillespie, J. Am. Chem. Soc. **47**, 305–312 (1925); *ibid.* **48**, 28–33 (1926); Phys. Rev. **34**, 352–366 (1929); *ibid.* **34**, 1605–1614 (1929); Chem. Rev. **18**, 359–372 (1936); J. A. Beattie, Phys. Rev. **31**, 680–690 (1928); *ibid.* **32**, 691–698, 699–705 (1928); *ibid.* **36**, 132–145 (1930); L. J. Gillespie and J. A. Beattie, Phys. Rev. **36**, 743–753, 1008–1013 (1930); *ibid.* **37**, 655 (1931); J. Am. Chem. Soc. **52**, 4239–4246 (1930).

[2] J. A. Beattie and O. C. Bridgeman, Proc. Am. Acad. **63**, 229–308 (1928).

[3] M. Benedict, G. B. Webb, and L. C. Rubin, J. Chem. Phys. **8**, 334–345 (1940).

[4] F. G. Keyes, J. Am. Chem. Soc. **49**, 1393–1403 (1927); F. G. Keyes and H. G. Burks, *ibid.* **50**, 1100–1106 (1928); E. Lurie and L. J. Gillespie, *ibid.* **49**, 1146–1157 (1927); H. T. Gerry and L. J. Gillespie, Phys. Rev. **40**, 269–280 (1932); J. A. Beattie, *ibid.* **51**, 19–30 (1929); J. A. Beattie and S. Ikehara, Proc. Am. Acad. **64**, 127–176 (1930); see also reference 1.

[5] B. H. Sage and W. N. Lacey, Ind. Eng. Chem. **31**, 1497–1509 (1939) [methane-ethane]; B. H. Sage, W. N. Lacey, and J. G. Schaafsma, *ibid.* **26**, 214–217 (1934) [methane-propane]; R. A. Budenholzer, B. H. Sage, and W. N. Lacey, *ibid.* **32**, 384–387 1262–1277 (1940) [methane-*n*-butane]; W. N. Lacey and B. H. Sage, private communication, [methane-isobutane]; W. B. Kay, private communication, [ethane-*n*-butane]; B. H. Sage and W. N. Lacey, Ind. Eng. Chem. **32**, 992–996 (1940) [propane-*n*-butane].

TABLE I. *Compositions of the three mixtures of methane and normal butane.*

SUBSTANCE	MASS, G	WEIGHT %	MOLES 1939 MOL. WEIGHTS[a]	MOLE % 1939 MOL. WEIGHTS[a]	MOLES 1928 MOL. WEIGHTS[b]	MOLE % 1928 MOL. WEIGHTS[b]	RATIO[c]
			Mixture A				
CH_4	0.8556	8.453	0.053334	25.066	0.053372	25.065	
n-C_4H_{10}	9.2667	91.547	.159438	74.934	.159559	74.935	
Total	10.1223		.212772		.212931		1.00075
			Mixture B				
CH_4	1.7778	21.928	.110819	50.436	.110899	50.435	
n-C_4H_{10}	6.3296	78.072	.108904	49.564	.108986	49.565	
Total	8.1074		.219723		.219885		1.00074
			Mixture C				
CH_4	2.5537	45.159	.159184	74.895	.159300	74.895	
n-C_4H_{10}	3.1012	54.841	.053358	25.105	.053398	25.105	
Total	5.6549		.212542		.212698		1.00073

[a] CH_4=16.0424; C_4H_{10}=58.121.
[b] CH_4=16.0308; C_4H_{10}=58.077.
[c] Ratio of total moles (1928 mol. wts.) to total moles (1939 mol. wts.).

cylinder as that used in the study of the critical constants and compressibility[6] of this substance. The two pure components were distilled several times at liquid nitrogen temperature to remove any air present. The *n*-butane was first distilled from the weighing bottle[7] into the bomb cooled in liquid nitrogen and then the methane transferred from a second weighing bottle. Correction was made for the small amount of methane left in the loading apparatus. The details of the compositions of the three mixtures are given in Table I. The equation of state constants for methane[2] and *n*-butane[6] were derived from data in which the density (mole/liter) was expressed in terms of 1928 atomic weights, while for the new data on the mixtures the 1939 atomic weights were used. The difference in the mole fractions assigned each mixture is insignificant but for all pressures *computed from the equation of state* the observed densities of the mixture must be multiplied by the factors given in the last column of Table I.

The experimental method for measuring the compressibility has been given elsewhere.[7] For the mixtures the steel bomb[7] was used.

EXPERIMENTAL RESULTS

In order to determine if appreciable decomposition had occurred at the higher temperatures, the pressures at several densities at 150°C were remeasured after the completion of the 300° isotherm. The results are given in Table II. A comparison of the pressures obtained before heating above 150° and after the completion of all of the runs shows that no decomposition had taken place, and gives an indication of the reproducibility of the measurements for a single leading.

In Tables III to V are given the experimental results of the present investigation. Our measurements barely overlap those of Budenholzer, Sage, and Lacey;[5] but such comparison as can be made indicates fair agreement.

THE EQUATION OF STATE FOR GAS MIXTURES

An equation of state that represents the compressibility of methane and *n*-butane and the values of the constants for these gases are given in Table VI. Let A_m represent any one of the

TABLE II. *Effect of decomposition on the measured pressure at 150°C.*

MIXTURE	DENSITY MOLE/LITER	PRESSURE, NORMAL ATMOS. AT TIME OF 150° RUN	AFTER 300° RUN	DIFFERENCE %
A	1.25	33.383	33.379	−0.012
	2.5	52.706	52.700	− .011
	5.0	79.300	79.295	− .006
B	1.25	37.726	37.746	+ .053
	2.5	67.213	67.238	+ .037
	5.0	118.581	118.601	+ .017
C	1.25	40.670	40.671	+ .002
	2.5	77.590	77.578	− .015
	5.0	148.499	148.437	− .042

[6] J. A. Beattie, G. L. Simard, and G.-J. Su, J. Am. Chem. Soc. **61**, 24–26, 26–27 (1939).
[7] J. A. Beattie, Proc. Am. Acad. **69**, 389–405 (1934).

TABLE III. *Compressibility of mixture A.*

DENSITY, MOLE/LITER* TEMP. °C (INT.)	1.25	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	6.0	7.0	8.0	9.0
	PRESSURE, NORMAL ATMOSPHERES												
125	29.88	33.72											
150	33.38	38.10	46.12	52.71	58.35	63.50	68.50	73.64	79.30	93.83	118.30	165.58	258.88
175	36.77	42.33	52.21	60.81	68.58	75.97	83.30	91.06	99.57	121.49	156.51	218.79	332.22
200	40.08	46.47	58.15	68.71	78.60	88.25	98.11	108.53	120.17	149.76	195.46	272.36	
225	43.35	50.57	64.00	76.50	88.51	100.46	112.81	126.11	140.92	178.47	234.84	326.38	
250	46.56	54.58	69.72	84.13	98.25	112.50	127.47	143.57		207.16	274.27		
275	49.75	58.55	75.43	91.74	107.96	124.55	142.06	161.07	182.39	235.96	313.90		
300	52.91	62.51	81.07	99.26	117.57	136.48	156.56	178.52	203.10	264.69			

* 1939 molecular weights.

TABLE IV. *Compressibility of mixture B.*

DENSITY, MOLE/LITER* TEMP. °C (INT.)	1.25	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	6.0	7.0	8.0	9.0	10.0
	PRESSURE, NORMAL ATMOSPHERES													
100	31.40	36.24												
125	34.61	40.25	50.54	59.83	68.37	76.42	84.30	92.18	100.29	118.58	140.30	170.37	214.98	284.73
150	37.73	44.14	56.11	67.21	77.67	87.80	97.84	107.98	118.58	142.04	171.22	210.53	266.72	352.38
175	40.84	47.99	61.57	74.42	86.76	98.90	111.08	123.55	136.62	165.90	202.23	250.71	319.09	
200	43.92	51.82	66.99	81.49	95.68	109.77	124.14	138.86	154.51	189.50	232.85	291.10		
225	46.99	55.61	72.33	88.61	104.70	120.79	137.31	154.51	172.71	213.81	264.80			
250	50.02	59.36	77.62	95.57	113.48	131.60	150.29	169.85	190.66	237.81	296.17			
275	53.02	63.08	82.87	102.50	122.23	142.36	163.24	185.18	208.55	261.77				
300	56.02	66.79	88.12	109.45	130.94		176.12		226.40					

* 1939 molecular weights.

TABLE V. *Compressibility of mixture C.*

DENSITY, MOLE/LITER* TEMP. °C (INT.)	1.25	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	6.0	7.0	8.0	9.0	10.0
	PRESSURE, NORMAL ATMOSPHERES													
75	31.90	37.50	48.07	57.91	67.18	76.03	84.58	92.97	101.34	118.23	136.53	157.25	181.85	212.60
100	34.86	41.15	53.16	64.57	75.50	86.09	96.47	106.78	117.12	138.49	161.79	188.22	219.73	258.73
125	37.77	44.73	58.18	71.12	83.68	96.02	108.22	120.48	132.89	158.78	187.12	219.55	258.08	305.37
150	40.67	48.30	63.15	77.59	91.78	105.82	119.85	134.04	148.50	178.92	212.48	250.86	296.39	351.90
175	43.56	51.83	68.06	84.02	99.78	115.53	131.34	147.43	163.93	198.84	237.51	281.90	334.47	
200	46.43	55.35	72.96	90.38	107.75	125.17	142.81	160.85	179.38	218.82	262.71	313.08		
225	49.30	58.87	77.85	96.74	115.68	134.79	154.23	174.18	194.78	238.73	287.89	344.28		
250	52.14	62.36	82.71	103.06	123.56	144.35	165.58	187.43	210.08	258.64	312.98			
275	54.99	65.86	87.56	109.37	131.42	153.90	176.91	200.68	225.37	278.48	338.06			
300	57.82	69.34	92.39	115.64	139.27	163.39	188.21	213.87	240.57	298.10				

* 1939 molecular weights.

TABLE VI. *Constants of the Beattie-Bridgeman equation of state for methane and normal butane.*

$$p = [RT(1-\epsilon)/V^2][V+B] - A/V^2$$
$$A = A_0(1-a/V) \quad B = B_0(1-b/V) \quad \epsilon = c/VT^3$$

GAS	R	A_0	a	B_0	b	c	MOL. WT
	Units: liter/mole, normal atmos., °K (T°K $= t$°C $+273.13$)						
CH_4	0.08206	2.2769	0.01855	0.05587	−0.01587	12.83×10^4	16.0308
n-C_4H_{10}	.08206	17.7940	.12161	.24620	+ .09423	350×10^4	58.077

TABLE VII. *Comparison of the pressures computed from the equation of state of mixtures with the observed pressures to a density of 5 mole/liter.*

Observed pressures given in Tables III to V.
Equation of state of mixtures same as that given in Table VI except each parameter is for the mixture: A_{0m}, a_m, B_{0m}, b_m, c_m.

Methods of combination of constants: see Eqs. (5), (6), and (7).

DESIGNATION	A_{0m}	a_m	B_{0m}	b_m	c_m
Method I	square-root	linear	linear	linear	linear
Method II	square-root	linear	linear	linear	square-root
Method III	square-root	linear	Lorentz	linear	linear
Method IV	square-root	linear	Lorentz	linear	square-root

Average percentage deviation of the calculated from the observed pressure

METHOD	MIXTURE A (64 POINTS)	MIXTURE B (72 POINTS)	MIXTURE C (90 POINTS)	ALL THREE (226 POINTS)
I	1.21%	1.44%	1.76%	1.50%
II	2.68	3.38	3.59	3.26
III	2.48	3.03	1.71	2.35
IV	0.59	0.65	0.92	0.74

parameters for the mixture. Then

$$A_m=\sum_i \sum_j x_i x_j A_{ij}, \quad (1)$$

where each summation extends over all of the components of the mixture, x is the mole fraction of a component in the mixture (V then being the volume of one average mole of mixture), $A_{ij}(j=i)$ is the constant for the ith component, and $A_{ij}(i\neq j)$ is an interaction constant characteristic of the encounter of unlike molecules. The three methods that have been used for computing the interaction constants are:

$$A_{ij}=\tfrac{1}{2}(A_{ii}+A_{jj}), \quad (2)$$

$$A_{ij}=A_{ii}^{1/2}A_{jj}^{1/2}, \quad (3)$$

$$A_{ij}=\tfrac{1}{8}(A_{ii}^{1/3}+A_{jj}^{1/3})^3. \quad (4)$$

When substituted into Eq. (1) these methods give, respectively:

$$A_m=\sum_i x_i A_i,$$

(linear combination of constants) (5)

$$A_m=(\sum_i x_i A_i^{1/2})^2, \quad \text{(square-root combination of constants)} \quad (6)$$

$$A_m=\tfrac{1}{8}\sum_i \sum_j x_i x_j (A_i^{1/3}+A_j^{1/3})^3,$$

(Lorentz combination of constants) (7)

where single instead of double subscripts are written to designate the constant for the pure components.

From the time of van der Waals square-root combination has been used for the A_0 constant of the equation of state arising from the attractive force between molecules, and Lorentz combination for the B_0 constant arising from the repulsive force. The latter corresponds to averaging collision radii and leads to much more complicated expressions than linear combination (averaging molecular volumes) which has often been used for B_0.

We have applied the four methods of combining constants shown in Table VII to our data. For each method the parameters for each of the three mixtures were computed by the proper one of Eqs. (5) to (7), by use of the compositions given in Table I and the constants for the pure components from Table VI, to yield an equation for the mixture of the same form of that for a pure gas. For each method we computed every pressure for each mixture given in Tables III to V from density 1.25 to 5.0 mole/liter, using for the density that given in the table multiplied by the factor given in the last column of Table I. The results are summarized in Table VII. The deviations are caused by two factors: failure of the equation of state to represent the properties of the pure components, and failure of the combination rule. The first was estimated by computing at each density the sum $\sum_i x_i\delta_i$ where x_i is the mole fraction of the ith component and δ_i is the average percentage deviation of the calculated from the observed pressure for the pure component. Estimated in this manner the deviations introduced by the failure of the equation to represent the properties of the pure gases amount to about half of those entered under method IV.

Method IV yields the best results; and it gives a satisfactory representation of the data to 5 mole/liter. Method I, which gives deviations about twice as great, is a good compromise between simplicity and accuracy. It is the method which has been most used in the past for computing[4] the properties of gas mixtures. As has been found earlier,[4] method I is superior to method III.

This work was greatly aided by a fellowship from the Polymerization Process Corporation. We thank the Buffalo Laboratory of the Linde Air Products Company, and the Southern California Gas Company for the gifts of the samples of methane and *n*-butane; and Drs. L. I. Dana, B. H. Sage, and M. Benedict for their help in procuring the samples.

The Crystalline Structure of Pt_3O_4

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(Received June 30, 1941)

By x-ray diffraction, the chemical formula and crystal structure of Pt_3O_4 have been established. The crystal lattice has a body-centered cube symmetry. The edges of the cubes are 6.226A long, and there are two molecules per unit cell. A chemical method for preparing this oxide has been given by Jörgensen but Wöhler claims that the compound thus obtained is a mixture of monoxide and dioxide rather than a separate chemical entity, see references 2 and 3.

INTRODUCTION

THE crystal structure of the platinum oxides has never yet been studied.[1] Neither has the chemical process used for their preparation been very clearly understood,[2,3] and in some cases even the existence of such platinum oxides has been doubted.[4] We have studied the crystalline structure of a compound formed on a platinum wire which has been used during 15 years in Duane's set up for the purification of radon. In this apparatus the wire was heated red hot to recombine oxygen and hydrogen. The available amount of the compound is very small and this fact makes its chemical analysis impossible, but the x-ray diffraction pattern is very neat and understandable. This compound is reduced to metallic platinum by heating it in the air. Using it as the cathode for the electrolysis of an aqueous solution of sulphuric acid, the nascent hydrogen reduces it to metallic platinum. Furthermore, in a report of Finch, Murison, Stuart and Thomson[5] it is pointed out that on some platinum plates heated in an atmosphere of oxygen, oxides were formed; and by electron diffraction they find, among the lines corresponding to platinum, other lines corresponding to spacings 4.4; 3.06; 2.06; 1.73 and 1.31A which correspond to the lines 1, 2, 5, 6, and 11 of our pattern.

These characteristics make us think that our compound is a platinum oxide. After the study of the x-ray diffraction pattern and the photometric measure of the intensities of its lines, we used Fourier's method to determine the coordinates of the oxygen atoms. On the basis of the results obtained we conclude that this compound must be Pt_3O_4, with two molecules per unit cell. The theoretical density is 8.8 g/cm³.

EXPERIMENTAL METHODS AND RESULTS

Figure 1 shows the Co-$K\alpha$ x-ray photograph made in a 28.85-mm radius Debye-Scherrer's camera. The lines 3′ and 14 only appear in some patterns and, besides being weak, their intensity

TABLE I. *Interpretation of powder photograph.*

Line No.	Indices	Spacings Obs.	Spacings Calc.	Structure Factors Obs.	Structure Factors Calc.	
1	110	4.400	4.402	− 31.3	− 37.2	
2	200	3.113	3.113	+ 77.2	+ 91.8	
3	211	2.552	2.540	− 25.8	− 33.4	
3′	—	2.275	—	—	—	111 of Pt
4	220	2.218	2.204	+110.7	+106.6	
5	310	1.987	1.967	− 28.5	− 31.0	
6	222	1.809	1.793	+ 58.5	+ 81.5	
7	321	1.653	1.662	− 24.8	− 29.1	
8	400	1.568	1.556	+ 91.0	+ 92.1	
9	{411} {330}	1.477	1.469	− 33.9	− 27.8	
10	420	1.399	1.388	+ 49.5	+ 76.4	
11	332	1.334	1.326	− 29.6	− 26.4	
12	422	1.277	1.270	+ 84.3	+ 83.2	
13	{431} {510}	1.225	1.220	− 35.0	− 25.2	
14	—	1.200	—	—	—	311 of Pt
15	521	1.140	1.139	− 21.2	− 24.3	
16	440	1.110	1.102	+ 75.9	+ 76.9	
17	{433} {530}	1.069	1.065	− 24.2	− 23.5	
18	{442} {600}	1.040	1.040	+102.1	+ 64.7	
19	{532} {611}	1.010	1.009	− 10.5	− 22.6	
20	620	0.984	.984	+ 71.9	+ 64.0	
21	541	0.959	.959	− 14.3	− 22.0	
22	622	0.936	.940	+ 37.4	+ 61.2	
23	444	0.915	.915	—	+ 68.6	

[1] W. J. Moore and L. Pauling, J. Am. Chem. Soc. **63**, 1392 (1941), reported a "highly probable" structure of PtO, by similarity with that of PdO.
[2] S. M. Jörgensen, J. prakt. Chem. **16**, 345 (1877).
[3] L. Wöhler, Zeits. f. Anorg. Chem. **40**, 423 (1904).
[4] A. Baroni, Atti Accad. Lincei **21**, 756 (1935).
[5] G. I. Finch, C. A. Murison, N. Stuart and G. P. Thomson, Proc. Roy. Soc. **A141**, 414 (1933).

FIG. 1. X-ray powder photograph of the unknown compound.

is not uniform all over their length as it is in the other lines; these spurious lines are due to the Pt of the wire on which the oxide was formed. When the oxide was scraped off, the lines of the pattern obtained showed the same characteristics as 3′ and 14, due to orientation of the platinum crystals.

All the other lines correspond to a body-centered cube structure, the length of the cube edge being 6.226A (Table I, columns 2 and 3). We have determined the relative intensities of the lines from the blackening in the photographic plate, using a recording microphotometer of the Zeiss type.

The structure factors have been computed from F. C. Blake's formula:[6]

$$I \propto p \cdot F_{hkl}^2 \cdot f(\theta) \cdot A \cdot e^{-2M},$$

where

p = multiplicity of the plane hkl

F_{hkl} = structure factor

A = absorption factor

e^{-2M} = temperature factor

$$f(\theta) = \frac{1+\cos^2 2\theta}{\sin^2 \theta \cdot \cos \theta}.$$

We took for A and e^{-2M} the values from Blake's paper for the curves given there for Pt. With these values and the measured intensities, we computed (from Blake's formula) the relative values of F. The signs, however, still remain indeterminate.

In order to determine the arrangement of the atoms in our crystal lattice, we first resort to Wyckoff's tables[7] in which we find that the only space groups which admit a body-centered lattice are: T^3, T^5, O^5, O^8, T_h^5, T_h^7, T_d^3, T_d^6, O_h^9, O_h^{10}.

As the platinum atoms are the heaviest, we must find an arrangement of these atoms that will give for the structure factors values approaching the experimental ones. We assume

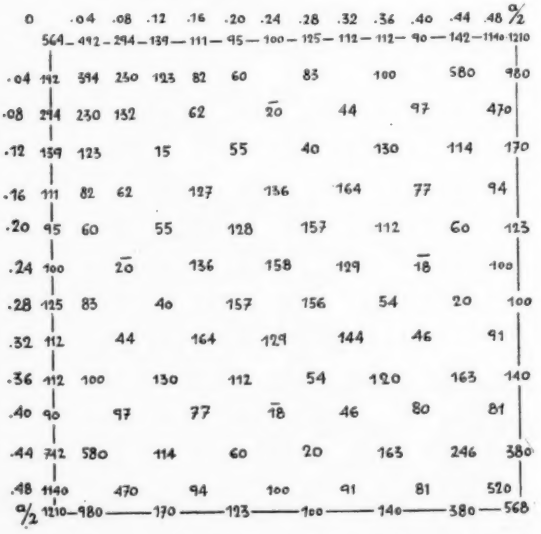

FIG. 2. Fourier projection on (001) values of 0.263ρ.

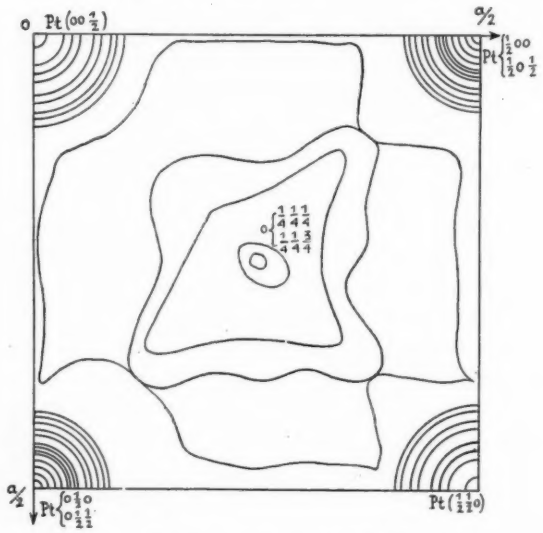

FIG. 3. Fourier projection on (001) lines of equal values of ρ.

[6] F. C. Blake, Rev. Mod. Phys. **5**, 169 (1933).

[7] R. G. Wyckoff, *Analytical Expression of the Results of the Theory of Space Groups* (1930).

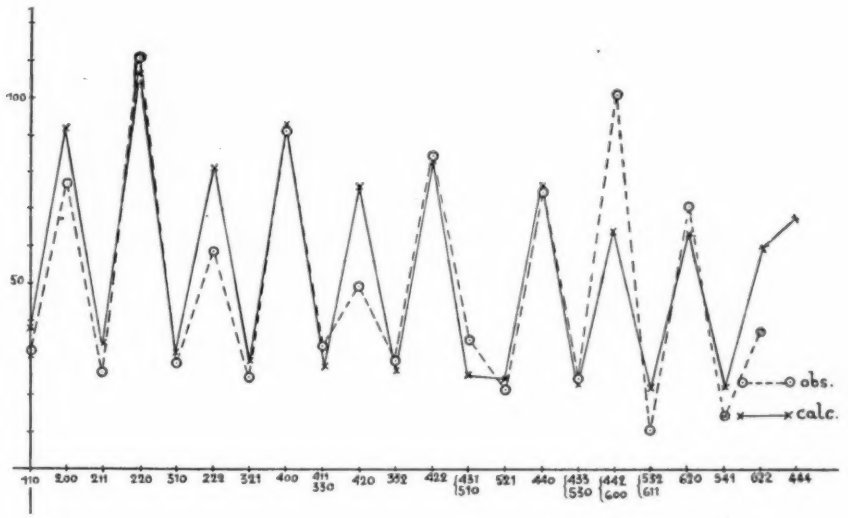

FIG. 4. Comparison of observed and calculated values of F_{hkl}.

that the presence of the oxygen atoms will only modify slightly the absolute value of the structure factor, without changing its sign. By trial, we found that the platinum atoms must occupy 6 equivalent positions in the arrangement noted as 6*e*, determined by the coordinates: $\frac{1}{2}00$, $0\frac{1}{2}0$, $00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$.

The theoretical structure factors for the assumed arrangement of the platinum atoms were calculated and the experimental values F_{hkl} were given the signs that were obtained. From the values of F_{hkl}, now known both in absolute value and sign, the values of the projections of the electron density on the 001 plane were obtained by Fourier's method.

Following Bragg and West[8] we used for our calculations the observed values F_{hk0} previously multiplied by the temperature factor $e^{-B \sin^2 \theta}$, in order to increase the convergence of the series. We have chosen $n=2$. Figures 2 and 3 show the results obtained, including F_{000} which was calculated after knowing the total number of atoms per unit cell. The figures show that, besides the maxima of electron density due to the platinum atoms at 6*e*, other maxima are apparent at $\frac{1}{4}, \frac{1}{4}; \frac{1}{4}, \frac{3}{4}; \frac{3}{4}, \frac{1}{4}; \frac{3}{4}, \frac{3}{4}$; which maxima correspond to the projection of 2 atoms of oxygen each. These atoms will therefore be located at the positions noted 8*e*, which coordinates are: $\frac{111}{444}$, $\frac{113}{444}$, $\frac{131}{444}$, $\frac{311}{444}$, $\frac{133}{444}$, $\frac{313}{444}$, $\frac{331}{444}$. A final check shows that the experimental structure factors agree fairly well with the ones calculated assuming 6 Pt atoms at 6*e* and 8 oxygen atoms at 8*e* per lattice (Table I, columns 5 and 6, and Fig. 4). Therefore, we assume as the most probable for the compound, the structure shown in Fig. 5 and the chemical formula Pt_3O_4.

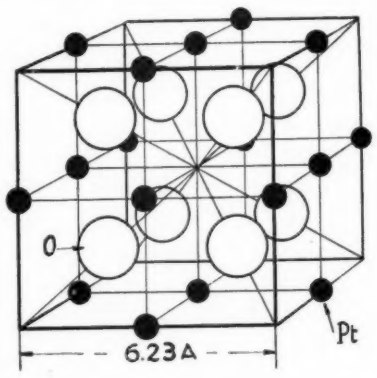

FIG. 5.

The distance between nearest atoms of Pt is 3.113A and that of Pt-O is 2.2A. From this data, the theoretical density is 8.8 g/cm^{-3}.

ACKNOWLEDGMENT

The authors are indebted to Prof. Dr. Isnardi, Dr. R. Busch, and Dr. J. T. D'Alessio for their constant interest and their suggestions during the preparation of this work, as well as to Dr. E. Gaviola for having kindly read the manuscript.

[8] W. L. Bragg and J. West, Phil. Mag. **10**, 823 (1930).

A Suggestion for a New Method of Fractionation of Proteins by Electrophoresis Convection

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(Received November 5, 1941)

IT is the purpose of the present note to suggest a new type of electrophoresis apparatus for the fractionation of proteins, based upon some of the principles of the thermal diffusion method employed in the separation of isotopes. In the thermal diffusion method, the separation of the components of a solution or gas mixture is effected by means of a differential horizontal transport arising from thermal diffusion, superimposed upon a vertical transport arising from convection in a canal connecting upper and lower reservoirs of the fractionating unit.[1] Separation of the components could also be obtained by differential horizontal transport in the canal through agencies other than thermal diffusion. For the fractionation of proteins in solution, we suggest the use of electrophoresis as the means of horizontal transport.

The proposed apparatus would consist of fractionating units of the following type to be employed individually for batch operation or in series for continuous operation. The individual fractionating unit may be schematically described as follows. Two reservoirs A and B are connected by a long vertical canal of length l, and cross section of thickness a, and breadth unity. Before operation the unit is filled with a homogeneous solution of two proteins, 1 and 2. A vertical convection current with a downstream in the vicinity of one wall of the canal and an upstream in the vicinity of the other is established by means of a temperature difference maintained between them. If feasible, the convection current might be established by a suitable pumping device rather than by a temperature gradient. For small temperature differences, hydrodynamics yields the following expression for the vertical convection velocity v_z of the fluid as a function of the horizontal distance X from the wall of lower temperature.

$$v_z=-\gamma[x^3-3x^2/2+x/2],$$
$$x=X/a, \quad \gamma=\frac{\beta\rho g a^2}{6\eta}\Delta T, \tag{1}$$

where g is the acceleration of gravity, ΔT the temperature difference, ρ, β, η the mean values of the density and coefficients of thermal expansion and viscosity of the solution in the specified temperature interval. An electric field E is applied in the horizontal direction imparting to each solute species a horizontal component of velocity,

$$v_x^{(i)}=u_iE+u_i^{(T)}dT/dX, \tag{2}$$

where u_i is the electrophoretic mobility of the protein component i and $u_i^{(T)}$ is its thermal diffusion mobility.

As a result of the horizontal and vertical components of velocity v_x and v_z, a net transport of each solute between the reservoirs A and B occurs. This transport is opposed by ordinary diffusion so that a stationary state corresponding to a definite concentration difference is ultimately reached. Due to differential horizontal transport of the two solute species depending upon the difference in their electrophoretic and thermal diffusion mobilities, different concentration ratios will be established for the two species and a separation effected.

Solution of the diffusion equations even for the stationary state is rather complicated. Only the first term in the expansion of the concentrations in a power series in the field intensity E has been carried out thus far. It is found that the concentration of each solute varies exponentially with height in the canal. The stationary value of the concentration ratio C_i^B/C_i^A of component i in the upper and lower reservoirs

[1] See for example, Furry, Jones, and Onsager, Phys. Rev. **55**, 1083 (1939).

A and B,

$$C_i^B/C_i^A = e^{\alpha_i},$$

$$\alpha_i = \frac{84l}{\gamma a}\left\{u_i E + u_i^{(T)}\frac{dT}{dX}\right\}. \tag{3}$$

$$\left.\begin{aligned}\left(\frac{\gamma a}{4D_i}\right)^2 &\gg 630\\ v_x^{(i)} a/D_i &\ll 1\end{aligned}\right\}, \tag{3a}$$

where D_i is the diffusion coefficient of component i. The first of conditions (3a) will generally be fulfilled, since convection velocities large relative to diffusion velocities are suitable for operation. By suitable choice of the sign of the electric field E, we can, insofar as pure thermal diffusion is to be neglected, transport a given species either up or down the canal. In order to avoid too serious a disturbance of the convection current during operation, it is desirable to select the sign of E so that the net transport of both species produces an increase in density in the lower reservoir and not in the upper one.

The stationary value of the separation factor, f_0, defined as $(C_1^B C_2^A)/(C_2^B C_1^A)$, when net transport takes place from reservoir A to reservoir B, is

$$f_0 = e^{\Delta\alpha},$$
$$\Delta\alpha = \alpha_1 - \alpha_2. \tag{4}$$

From Eqs. (3) and (4) it would appear that, subject of course to condition (3a), smaller convection velocities favor the separation. This is reasonable, since if the convection velocity is too great relative to the horizontal velocity, transport of the solute species from the downstream to the upstream will not have time to take place to any great extent in one trip of the fluid through the canal.

Slower convection velocities of course increase the time necessary to approach the stationary state. Neglecting the transient contribution to the vertical transport, we find that the time t_r, required for a concentration ratio r, equal to C_i^B/C_i^A to be attained, when reservoir A is so large that C_i^A remains effectively constant, is

$$t_r = \frac{10^4 V_B D_i l}{\gamma^2 \alpha_i a^3}(e^{\alpha_i} - 1)\log\left(\frac{e^{\alpha_i} - 1}{e^{\alpha_i} - r}\right). \tag{5}$$

where V_B is the volume of reservoir B. This calculation could be improved by methods similar to those of Debye[2] and Bardeen.[3] It may seem strange that t_r is proportional to the diffusion constant D_i. However, under conditions (3a) only horizontal diffusion is important, and approach to equilibrium is retarded by rapid diffusion.

Rough calculations based upon Eqs. (3) and (4), indicate that significant separations should be attainable in periods of time of the order of several days with applied fields of the order of 0.1 volt/cm, electrophoretic mobility differences of the order of 10^{-5} cm²/volt sec., and diffusion constants of the order of 10^{-6} cm²/sec., with the use of canals one meter in length and one millimeter in thickness across which temperature differences of the order of one degree are maintained.

A preliminary experimental investigation of the method with mixtures of ovalbumin and hemoglobin has been carried out at the Rockefeller Institute for Medical Research by Dr. Shedlovsky and Dr. Hoagland. In their apparatus, the walls of the canal consist of Cellophane membranes permeable to buffer but impermeable to the proteins and the canal is immersed in an external buffer solution containing the electrodes producing the electric field. The preliminary experiments indicate that significant separation is realized, but a systematic investigation of the various factors influencing the separation has not yet been made.

[2] P. Debye, Ann. d. Physik **56**, 284 (1939).
[3] J. Bardeen, Phys. Rev. **57**, 35 (1940).

Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Immobile Layer at the Solid-Liquid Interface

J. J. BIKERMAN
68 Grange Road, London W. 5, England
September 29, 1941

IN a paper just published by Eversole and Lahr[1] the first calculations are made of the thickness t of the "immobile layer of . . . solution at the solid-liquid interface." The idea of such a layer was introduced by Freundlich to account for the observed discrepancy between the "electrochemical" potential, e.g., that of a glass electrode, and the "electrokinetic" potential, e.g., that responsible for cataphoresis of a glass particle. O. Stern[2] has identified this layer with that of adsorbed ions; his view seems to be widely held. Eversole and Lahr envisage a "rigid multilayer" inclosing part of the counter-ions.

No explanation has so far been advanced for the existence of this immobile layer. It has no place in the usual hydrodynamics or in the usual electrostatics. No mechanism has been suggested which would prevent ions and/or water molecules from moving along the solid surface. It seems very probable that no such mechanism exists and that all ions and molecules near the solid-liquid interface are free to move according to ordinary physical laws.

But an immobile layer exists and is simply due to the roughness of all solid surfaces. If Fig. 1 is the profile of a surface (magnified some 10^5 or 10^6 times) it is obvious that the liquid below the level AA can hardly participate in the movement of the bulk of liquid. The average distance between the plane AA and the actual surface is the thickness t of the immobile layer. Calculation from electrokinetic data gives for t the order of magnitude 10^{-7} to 10^{-6} cm, a quite probable range for smooth glass or porcelain surfaces.

Contrary to the hypotheses of immobilized ions or a rigidity layer, which apparently cannot predict a relation between the magnitude of t and the properties of the solid surface, the interpretation forwarded here requires a direct effect of the surface roughness on the value of t. I was engaged in seeking in literature an evidence for this effect when Eversole and Lahr's paper appeared.

When computing t Eversole and Lahr provisionally

FIG. 1.

assumed the total potential difference betwcen interfaee and bulk of solution to be constant. It should be emphasized that the order of magnitude of t remains unchanged even if a considerable variation of the total potential difference with concentration is admitted.

[1] W. G. Eversole and P. H. Lahr, J. Chem. Phys. **9**, 530 (1941).
[2] O. Stern, Zeits. f. Elektrochemie **30**, 508 (1924).

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